

AFML-TR-68-181  
PART II

# KINETIC ANALYSIS OF THERMOGRAVIMETRY

## PART II. PROGRAMMED TEMPERATURE

IVAN J. GOLDFARB

ROBERT McGUCHAN

ALAN C. MEEKS

TECHNICAL REPORT AFML-TR-68-181, PART II

DISTRIBUTION STATEMENT A

Approved for public release;  
Distribution Unlimited

19960516 050

DECEMBER 1968

DEPARTMENT OF DEFENSE  
PLASTICS TECHNICAL EVALUATION CENTER  
PICATINNY ARSENAL, DOVER, N. J.

This document has been approved for public  
release and sale; its distribution is unlimited.

AIR FORCE MATERIALS LABORATORY  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

THIS QUALITY ASSURED

PLASTEC

122222

## **NOTICE**

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This document has been approved for public release and sale; its distribution is unlimited.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AFML-TR-68-181  
PART II

## KINETIC ANALYSIS OF THERMOGRAVIMETRY

### PART II. PROGRAMMED TEMPERATURE

*IVAN J. GOLDFARB*  
*ROBERT McGUCHAN*  
*ALAN C. MEEKS*

This document has been approved for public  
release and sale; its distribution is unlimited.

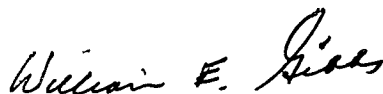
## FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules," with Dr. I. J. Goldfarb (MANP) acting as task scientist. The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

The authors wish to thank Mr. W. T. Baltzell and Mr. R. R. Luthman, Jr., for their aid in collection and analysis of the data.

This report covers research conducted from January 1967 to May 1968. The report was submitted by the authors in July 1968 for publication as a technical report.

This technical report has been reviewed and is approved.



WILLIAM E. GIBBS  
Chief, Polymer Branch  
Nonmetallic Materials Division  
Air Force Materials Laboratory

# ABSTRACT

A generally applicable method of obtaining kinetic parameters from temperature-programmed thermogravimetry is presented. Factors influencing the selection of a particular method for the numerous treatments reported in the literature are discussed in detail. The method of Friedman involving the use of several thermograms at different heating rates and determining Arrhenius parameters at each percent conversion was chosen. The experimental procedure and a method of handling thermogravimetric analysis (TGA) data and calculations by computer are fully described. The application of the treatment to some specific polymer degradation systems is reported in order to illustrate the scope of the method and its potential usefulness in obtaining information concerning complex degradation mechanisms. Poly(tetrafluoroethylene), an aliphatic, and an aromatic polyamide were the polymers selected for this study.

TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II DISCUSSION	2
1. General Considerations	2
2. Kinetic Analysis of Programmed Weight-Loss Data	6
3. "Friedman" Method of Analysis	11
4. Significance of Kinetic Parameters	15
III EXPERIMENTAL PROCEDURE	16
1. Polymer Samples	16
2. Apparatus	16
3. Temperature Measurement	16
4. Procedure	18
IV COMPUTER HANDLING OF THERMOGRAVIMETRIC ANALYSIS DATA	19
1. Computation of Rate of Weight Loss	19
2. Computation of Arrhenius Parameters	23
V WEIGHT LOSS OF POLY(TETRAFLUOROETHYLENE)	27
1. Variation of Activation Energy With Conversion	29
2. Order of Reaction	33
3. Pre-Exponential Factor	33
4. Discussion	33
VI DEGRADATION OF OTHER POLYMERS	34
1. Poly (1,4-phenylene sebacate)	34
2. Poly (hexamethylene sebacamide), Nylon 6.10	40
VII CONCLUSIONS	43
REFERENCES	44

TABLE OF CONTENTS (CONT)

SECTION		PAGE
APPENDIX I	Typical Input Card Deck	47
APPENDIX II	Complete Rate of Weight Loss Program	49
APPENDIX III	Punched Card Output From Rate Program	55
APPENDIX IV	Complete Program for the Determination of Arrhenius Parameters by Friedman's Method	57
APPENDIX V	Rates of Weight Loss for a Typical Teflon Experiment	63
APPENDIX VI	Rates of Weight Loss of Teflon Under Various Heating Rates	69
APPENDIX VII	Computer Printout of Activation Energy Results for Teflon Degradation	73

## ILLUSTRATIONS

FIGURE	PAGE
1. Weight and Rate of Weight Loss as a Function of Temperature	7
2. Typical Thermogram	20
3. Schematic Representation of Rate of Weight Loss Calculations	24
4. Schematic Representation of Arrhenius Parameter Calculations	26
5. Arrhenius Plot for Degradation of Teflon at 50% Weight Loss	30
6. Variation of Activation Energy with Conversion for the Weight Loss of Teflon	31
7. Log A F(W) Curves for Teflon Degradation	32
8. Rate of Weight Loss of Poly(1,4-phenylene sebacate) as a Function of Weight Loss	35
9. Activation Energy as a Function of Weight Loss for Degradation of Poly(1,4-phenylene sebacate)	37
10. Log A F(W) Curves for Overall and Component Reactions in the Degradation of Poly(1,4-phenylene sebacate)	38
11. Separation of Rate of Weight Loss/Temperature Curves	39
12. Activation Energy for Weight Loss of Nylon 6.10	41
13. Log A F(W) Curve for the Weight Loss of Nylon 6.10	42

## TABLES

TABLE	
I	Kinetic Methods for Programmed TGA 8
II	Effect of F(W) on Log A F(W) Plot 12
III	Identification Card 21
IV	Contents of Data Cards 22



## SECTION I

### INTRODUCTION

A knowledge and understanding of polymer degradation processes is necessary to improve the performance of polymers in high temperature applications and to direct research towards more thermally stable systems. One of the most important methods of studying polymer degradation is to examine the kinetics governing the breakdown reactions from which information about the thermal stability and the mechanism of degradation can be obtained.

In degradation kinetics, the rate of change of some property must be measured as a function of time, temperature, or conversion; any of several properties can be utilized if the property can be correlated with the degradation process, e.g., mass, molecular weight, a chemical group, or production of volatile products. A common method has been to follow weight changes. A thermobalance can be used to continuously record the weight changes. In the past, isothermal studies have been most common, in which the sample is maintained at a constant temperature while weight-time measurements are made. In recent years, temperature-programmed methods have been increasingly used. In this method, temperature is continuously raised, usually linearly with time, and a thermogram of weight versus temperature obtained. In theory, the programmed method should have certain advantages over the isothermal method. An important criticism of isothermal methods is that the temperature of the sample cannot be raised instantaneously to the desired temperature so that some weight may be lost before the degradation temperature is reached. This weight loss may give rise to an apparent maximum in the rate curve which masks the true initial features. Initial rate characteristics are very important since end-group and impurity-induced reactions may show up. Temperature-programmed methods should overcome this problem. It was further visualized that since weight-temperature dependencies were contained in a single chart the thermogram from a programmed experiment would yield the equivalent information of a large family of isothermal experiments. Thus, sample uniformity errors would be avoided and the procedure would be less time consuming. The thermograms are also useful for qualitative comparisons of thermal stabilities.

In this report, some of the numerous methods of obtaining kinetic parameters from programmed TGA are discussed. The methods are evaluated against the criteria that the method should be generally applicable, should give meaningful kinetic parameters, and should shed light on the mechanism of degradation. The selection of such a method and its application to some polymer systems is also described.

## SECTION II

### DISCUSSION

#### 1. GENERAL CONSIDERATIONS

The classical kinetic expression which is widely applicable to gas-phase and solution reactions is represented by Equation 1

$$\frac{-dC}{dt} = k F(C) \quad (1)$$

C = concentration of reactant

t = time

k = rate constant

F(C) = function of C

In classical kinetics, F(C) can often be expressed as a power function,  $C^n$ , for which n is defined as the order of reaction. The rate constant is temperature dependent and is defined by the Arrhenius equation

$$k = A e^{-E_a/RT} \quad (2)$$

- A = pre-exponential factor  
 $E_a$  = activation energy  
R = general gas constant  
T = absolute temperature

The normal kinetic approach is to determine rate constants for a given reaction at various temperatures using Equation 1 or an integrated form of it and thence to calculate the parameters A and  $E_a$  from Equation 2. The activation energy can often be correlated with the breaking of specific chemical bonds and gives important information concerning the mechanism of the reaction being studied.

Polymer degradation kinetics are normally studied in the solid or melt phase and, since a chemical reaction is occurring, it is assumed that a kinetic treatment and rate expression is applicable. Owing to the complexity and variety of polymer decomposition schemes, it is found, however, that the concentration of polymer molecules is not equivalent to the concentration of reactant in normal reactions so that the term "concentration" must be used with extreme caution in discussing polymer degradation. Two well established types of degradation illustrate this point (Reference 1). In the first, degradation is initiated at a chain end and proceeds by unzipping through the entire polymer chain. The sample loses one polymer molecule and its corresponding weight and volume, but the concentration of polymer molecules remains unchanged. In the second type, the elimination of side-groups in the chain alters the chemical structure of the polymer but does not necessarily influence the number or concentration of polymer molecules. In polymers, discussion in terms of reactive sites which could be chain ends, particular bonds or groups in the structure, the links joining monomer units, etc., is often more fruitful for elucidation of mechanisms.

It is found in practice that most degradation reactions result in loss of weight owing to the formation of smaller, volatile species [rearrangements such as the coloration of poly(acrylonitrile) are notable exceptions]. Therefore, it has been found convenient to study kinetics in terms of weight loss; to this extent, the approach is empirical since the only proof of validity is that experimental results appear to fit the adopted kinetic expressions. In order to preserve a close resemblance to normal kinetic procedure, the weight terms

should be expressed in fractional form. Further, since a reactant should have zero concentration on completion of reaction, the weight term should be corrected for any residue weight remaining after degradation. A general rate expression based on weight terms can now be postulated

$$-\frac{1}{W_o - W_f} \frac{dW}{dt} = k F \left( \frac{W - W_f}{W_o - W_f} \right) = k F(W) \quad (3)$$

$W$  = instantaneous weight of sample

$W_o$  = initial weight of sample

$W_f$  = final or residue weight

$\frac{W - W_f}{W_o - W_f}$  = fractional weight remaining

$(1 - \frac{W - W_f}{W_o - W_f}) = \frac{W_o - W}{W_o - W_f}$  = fractional weight loss

Equation 3 is equivalent to that used by Doyle (Reference 2) except that weight terms are retained here in preference to Doyle's active weight fraction,  $h$ . It must be emphasized that the functionality  $F(W)$  need not be simple and should not be assumed in advance. The presumption of "order" type functionality should be avoided unless it is warranted by experimental evidence. Two particular forms of  $F(W)$ , which have been observed in isothermal studies, merit a brief discussion at this point:

a.  $F(W) = \frac{W}{W_o}$  (for simplicity, assume  $W_f = 0$ )

This is a common case which results in apparent first order kinetics by analogy to classical rate laws. The rate of weight loss is proportional to the residual weight of polymer. Polymers which degrade predominantly by unzipping show kinetics of this type, the weight loss being a direct measure of the amount of unzipping and degree of degradation. This, of course, is a simplified view of the overall kinetics, and many other interesting kinetic dependencies can be observed (References 1 and 3).

b.  $F(W) = (L - 1) \frac{W}{W_o} - (1 - \alpha)^L \cdot \frac{(N - L)(L - 1)}{N} \quad (4)$

## Part II

$L$  = smallest chain length which does not evaporate under degradative conditions

$N$  = initial chain length of polymer

$\alpha = 1 - e^{-kt}$  (temperature constant) = degree of degradation (bond scission)

This complex form of  $F(W)$  has been developed by Simha et al as the solution to the random type of degradation mechanism (References 4 and 5). This mechanism consists of chain rupture taking place randomly; the act of scission need not result in weight loss which is possible only when scission occurs near a chain end to give a chain fragment of length  $< L$ . The rate of weight loss, corresponding to a spectrum of products of chain length from one to  $L$ , is proportional to the number of chain ends in the system, which increases at first owing to the random scission of the chains. Eventually, the average chain length becomes small enough that further increase in the number of ends is balanced by loss through evaporation. The rate of weight loss passes through a maximum and subsequently falls; it has been shown theoretically that the maximum should occur at approximately 26% conversion. Polymethylene and poly(methyl acrylate) are examples of vinyl polymers exhibiting the above features. Many condensation type polymers such as cellulose, polyamides, and polyesters also show random characteristics (Reference 3).

As has been discussed, several functionalities of weight are readily observed in isothermal weight-loss studies. In contrast, primary data from programmed TGA studies is much less revealing and differences caused by changes in weight functionality may be very subtle. The weight-temperature thermogram and the derivative rate-temperature curve (Figure 1) are somewhat general in character, apart from the obvious difference between a simple and multistep process; differences in shape are relative and could be divined only by reference to other "known" curves. That both activation energy and mechanism affect the shape of the curve adds to the difficulties (Reference 6). As is shown in this reference, rate-conversion curves are of greater diagnostic importance, although in practice, experimental fluctuations from a smooth curve might easily mask the diagnostic features, namely the conversion for the maximum rate and the initial slope of the curve. The ability of kinetic analysis to afford not only the Arrhenius parameters but also supplementary information about the mechanism is investigated in the following paragraphs.

## 2. KINETIC ANALYSIS OF PROGRAMMED WEIGHT-LOSS DATA

Analytical methods can be broadly divided into those using differential and integral treatments. Differential methods are based on Equation 3. In programmed TGA,  $k$  in this equation becomes a variable since temperature and therefore the rate constant are continuously changing. The expression can be rearranged as shown for a linear heating rate,  $B$ ,

$$B = \frac{dT}{dt}$$

$$\therefore -\frac{1}{W_0 - W_f} \cdot \frac{dW}{dT} = \frac{A}{B} \cdot e^{-E_a/RT} F(W) \quad (5)$$

The integral approach was developed to use TGA weight-loss data directly and to avoid calculation of rates. The equation of the thermogram (References 2 and 7) is obtained by integrating Equation 5

$$\int_{W_0}^W - \frac{dW}{(W_0 - W_f) F(W)} = F'(W) = \frac{A}{B} \cdot \int_{T_0}^T \exp \left( \frac{E_a}{RT} \right) dt \quad (6)$$

The result is given as

$$F'(W) = \frac{AE_a}{BR} p \left( \frac{E_a}{RT} \right) \quad (7)$$

in which  $p(E_a/RT)$  is a complex integral. In practice, integral methods use some convenient approximation based on Equation 7.

A detailed critique of all the previously reported kinetic treatments is beyond the scope of this report. Several reviews have been published (References 2, 8, and 9) and the recent paper by Flynn and Wall (Reference 6) offers an excellent critical survey of many of the methods. It is fitting, however, to examine some of the approaches and evaluate their usefulness for obtaining meaningful information about the degradation. Some representative approaches are listed in Table I. It is found that almost all the methods are subject to one or more of the following criticisms:

a. The equation fits a limited portion of the curve so that parameters for the whole degradation range cannot be obtained.

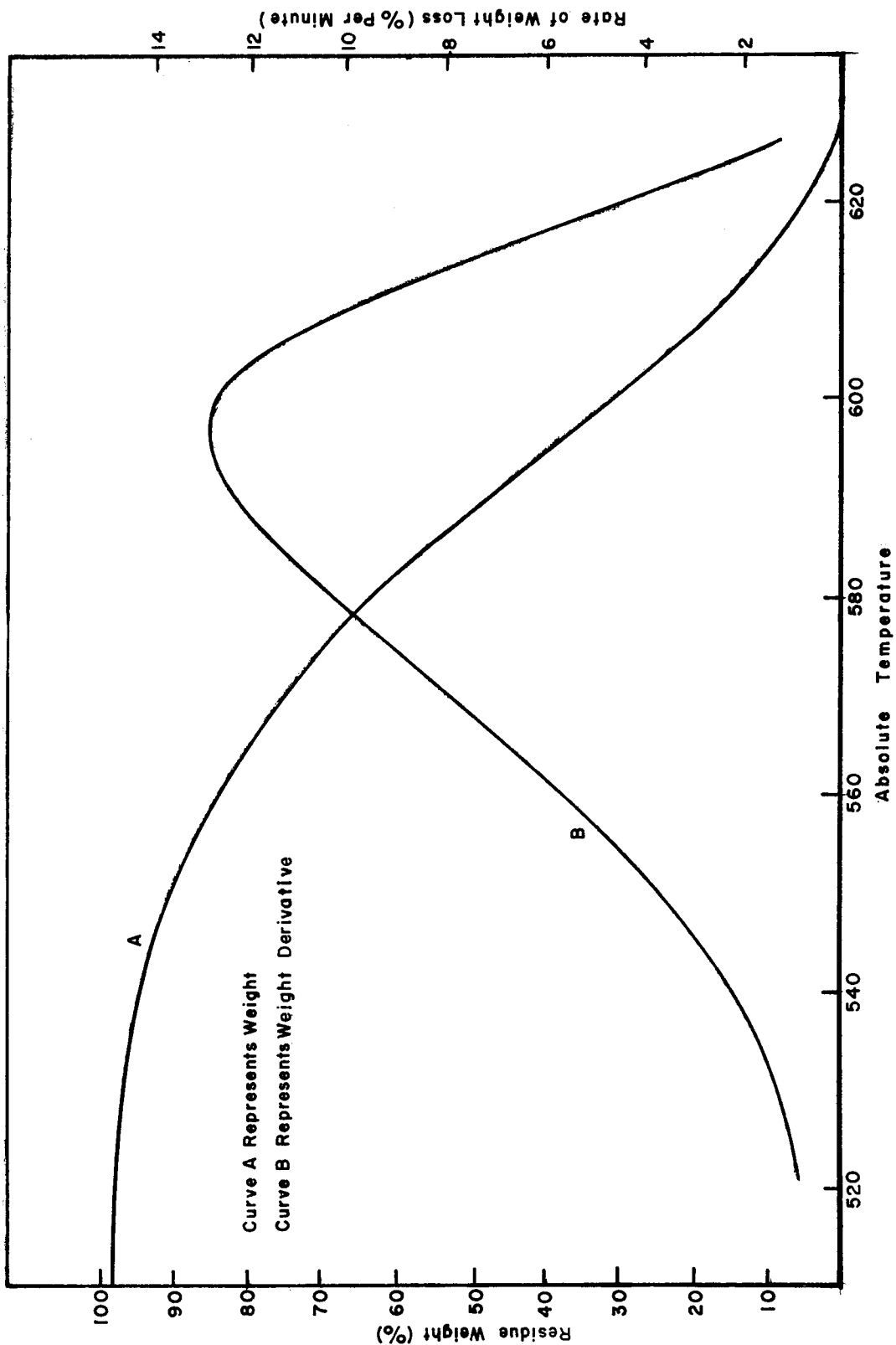


Figure 1. Weight and Rate of Weight Loss as a Function of Temperature

TABLE I  
KINETIC METHODS FOR PROGRAMMED TGA

DIFFERENTIAL	TYPE	EQUATION	AUTHOR	REFERENCE
	Single Point	$E_a = - \frac{RT_{\max}^2 \left( \frac{dW}{dT} \right)_{\max}}{W_{\max}}$	Fuoss, et al	10
	Single Curve	$\Delta \log(\text{rate}) = n \Delta \log W - \left( \frac{E_a}{2.3R} \right) \Delta \left( \frac{1}{T} \right)$	Freeman, Carroll Anderson, Freeman	11 12
	Single Curve	$\log(\text{rate}) = \log A + \frac{E_a}{R} \left[ \frac{W_{\max}}{T_{\max}^2 (\text{slope}_{\max})} \log W - \frac{1}{2.3RT} \right]$	Reich, Levi, Lee	13
	Different Initial Weights	$n = \frac{\log \text{rate}_1 - \log \text{rate}_2}{\log W_1 - \log W_2}$	Chatterjee	14
	Several Thermograms (Heating rate (B) varying)	$\log \text{rate}_B = \log A + \log F(W) - \frac{E_a}{2.3RT_B}$	Friedman	15
	Initial Part of Curve	$\log \frac{1-(W/W_0)}{T^2} = \log \frac{AR}{BE_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{E_a}{2.3RT}$	Coats, Redfern	16
	Area Under Initial Curve	$\text{Ln}(\text{Area}) = \frac{E_a}{RT} + \ln \left[ \left( \frac{R}{E_a} \right)^2 \cdot \frac{A}{B} \right]$	Reich, Levi	17
	Single Curve (Curve Fitting)	Equation 7 and calculated tables of $p(E_a/RT)$	Doyle	2,7
	Single Curve	$\text{LnLn}_n(W/W_0) = \frac{E(T-T_s)}{RT_s^2}, \quad T_s = T \text{ at } W/W_0 = 1/e$	Horowitz, Metzger	18
	Single Curve	$\log \frac{F'(W)}{T^2} = - \frac{E_a}{2.3R} \frac{1}{T} + \log \left[ \frac{r_2 RA}{BE_a} \right]$	Farmer	19
		( $r_2$ = error factor for approximate solution of integral)		
	Two Heating Rates	$E_a = 4.6 \log \left[ \frac{B_2}{B_1} \left( \frac{T_1}{T_2} \right)^2 \right] / \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$	Reich	20
	Several Heating	$\log B_1 + 0.457 \frac{E_a}{RT_1} = \log B_2 + 0.457 \frac{E_a}{RT_2}$	Ozawa	21



b. Degradation kinetics are assumed to be of the "order" type, and perhaps even first order kinetics are specified. Since, as has been previously discussed, this assumption is not necessarily valid, it is impossible to conclude whether the resulting parameters are meaningful. Often a random type degradation and probably other types will give a deceptively good fit to the first order approximation over most of the conversion range. Errors in assumed order, however, give vast errors in the other kinetic parameters; thus, in Reference 6, a random curve corresponding to an activation energy of 60 kcal-mole<sup>-1</sup> was analyzed by a first order treatment to have an activation energy ranging from 66 to 175 kcal-mole<sup>-1</sup> depending on conversion.

c. The time saving advantage of single point and single curve methods is obvious but it cannot be overemphasized that such analyses, when applied to a new system of unknown kinetics, may be absolutely worthless with regard to significant kinetic parameters.

d. Care must be taken when deriving approximate solutions since a sequence of steps involving successive approximations may give a final working equation which is not particularly applicable. Assumptions and approximations should be kept to a minimum.

On this basis, methods involving a single thermogram can be discarded and the potential of methods using several thermograms examined. The method of Reich using two heating rates (Table I) is unsatisfactory since no information about the rate law can be obtained. Chatterjee's method involving different sample weights must also be discarded since, in addition to the assumption of order, the reasoning is erroneous (Reference 37). When weight terms are expressed in the proper fractional units, his treatment collapses completely. In the equation for order (Table I), it can be visualized that "n" would always be unity, irrespective of the mechanism of degradation, excepting the possible influence of experimental irreproducibility and diffusion controlled weight loss.

Therefore, the choice of methods is reduced to two, one integral and the other differential; both require a series of thermograms to be obtained using

different heating rates and appear to be similar in potential and general applicability. This also represents the conclusion of the Flynn and Wall survey. In this report, selectivity was carried one stage further according to the following arguments:

a. In the past, integral methods have had the advantage that tedious manual derivations of rates of weight loss could be avoided. Since many thermobalances now incorporate automatic differentiation which allows simultaneous recording of TGA and differential thermogravimetry (DTG) curves and since, lacking this equipment, rates can be computed from weight-loss data (see Section III), differential methods need no longer be avoided.

b. The integral treatment involves more approximations than the differential method. Thus, the complex integral is normally approximated to a convenient working equation.

c. The integral treatments assume a linear heating rate throughout the degradation. This assumption is not strictly valid since, for example, volatilization of gaseous products produces a cooling effect on the polymer and a lowering of the heating rate.

d. In order to determine the rate law dependence,  $F(W)$ , in the integral method, experimental curves must be fitted to theoretical curves for known kinetic schemes. Experimental errors and kinetic irregularities (the latter are often observed during the initial and final stages of weight loss) would create difficulties in curve fitting. A more serious disadvantage is that the true kinetic scheme might be different from the available theoretical ones, e.g., the isothermal rate curve maximum at 40% conversion for polystyrene (Reference 22). In the study of the complex condensation polymers currently being used for high temperature applications, new types of rate dependencies may well appear and would necessitate laborious trial and error curve fitting in the integral method.

### 3. "FRIEDMAN" METHOD OF ANALYSIS

The foregoing arguments resulted in the selection of the method first used by Friedman (Reference 15). The basic equation used is shown in Table I and is the logarithmic expression of Equation 3

$$\log \left[ \frac{1}{(W_o - W_f)} \cdot \frac{dW}{dt} \right]_B = \log A + \log F(W) - \frac{E_a}{2.303RT_B} \quad (8)$$

Equation 8 denotes that both the rate and temperature corresponding to any specific value of  $F(W)$  are dependent on the heating rate employed. If it is assumed, for the moment, that the chemistry of the process is independent of temperature, then  $F(W)$  will be constant at any weight loss,  $\frac{W_o - W}{W_o - W_f}$ , regardless of heating rate. Thus, by measuring or calculating the rates and temperatures corresponding to the same fractional weight loss in a series of thermograms obtained at different heating rates and by plotting  $\log(\text{rate})$  against reciprocal temperature, the activation energy can be calculated for any conversion. An examination of the changes in calculated activation energies over the whole conversion range reveals whether the kinetics vary with conversion although it may be difficult to resolve experimental errors and real changes in activation energy. If the activation energy does not vary much over the entire range, an average value,  $\bar{E}_a$ , is calculated. Hence, by rearranging Equation 8

$$\log A F(W) = \log A + \log F(W) = \log(\text{rate})_B + \frac{E_a}{2.303RT_B} \quad (9)$$

Values of  $\log A F(W)$  are calculated at each conversion for the various heating rates. Theoretically, there should be no heating rate variation,  $A$  and  $F(W)$  being considered to be independent of temperature in the simple case, but experimental errors usually result in a small spread of  $\log A F(W)$  values so that an average value is again calculated.

When this process has been repeated for all conversions, a plot of  $\log A F(W)$  against  $\log \frac{W}{W_o}$  (or  $\log \frac{W - W_f}{W_o - W_f}$  for degradations producing a residue) reveals the rate law. In the programmed TGA method, this plot removes the effect of heating rate and changing temperature; for diagnostic purposes, it is analogous to the rate-conversion curve in isothermal treatments. In many cases, therefore, the appropriate weight functionality will be elucidated (Table II).

TABLE II  
EFFECT OF F(W) ON LOG A F(W) PLOT

F(W)	LOG A F(W) PLOT
$\frac{W}{W_o} ; \frac{W - W_f}{W_o - W_f}$	straight line, slope = 1
$\left( \frac{W - W_f}{W_o - W_f} \right)^n$	straight line, slope = n
"random" function	curve, maximum at log(0.74) (26% conversion)

Other types of kinetics, such as those giving a rate maximum at conversions other than 26%, would be just as easily resolved by this plot. Kinetic irregularities are revealed; for example, early weight loss caused by lower activation energy processes normally shows as a steeply falling portion in the initial stages of the log A F(W) curve. In fact, any true change in the kinetics will produce a change in slope of the plot based on the assumption of a single activation energy process. The extreme sensitivity of log A F(W) to changes in  $E_a$  explains why an average  $E_a$  is used instead of individual values at each conversion. If the latter were used, the experimental fluctuations of  $E_a$  would outweigh the effect of rate on log A F(W); the resulting plot would be very scattered and no information about the weight functionality would be obtained. Other potential sources of error in determining the form of F(W) are wrongly assigned conversion ranges and use of wrong conversion units. These may seem obvious but the former can be easily done in some complex thermograms and the latter follows from perusal of the variety of expressions used in the past. For example, in the original description of this method, Friedman used a different expression of concentration,  $\left( \frac{W - W_f}{W_o} \right)$ , from that proposed in this report. The result was a very high apparent order of reaction.

The pre-exponential factor can be easily calculated by subtracting the F(W) value from the log A F(W) term. The determination of A could be accomplished graphically by replotting log A F(W) against log F(W) and extrapolating the resulting straight line to log F(W) = 0. The ability of the method

to completely analyze more complex degradation systems with some typical complicating features is discussed in the following paragraphs.

a. Activation energy changes with conversion

Certain degradation mechanisms involve real activation energy changes with conversion (References 3 and 5). The reason may be a dependence of  $E_a$  on the molecular weight which itself varies with conversion, a change in mechanism as in poly(methyl methacrylate), or a change in structure of the polymer. Suppose a smooth increase in  $E_a$  is observed in the  $E_a$ -conversion plot obtained by the preceding analysis. The assumption of an average  $E_a$  to calculate  $\log A F(W)$  would invalidate the rate law determination. Features such as rate maxima would still be discerned but the overall curve would be skewed relative to the "theoretical" curve. Then, it is conceivable that a smooth  $E_a$  profile might be used instead of an average  $E_a$  to give more meaningful information about  $F(W)$ .

b. Random Degradations

The complex functionality of weight for this mechanism (Equation 4) casts doubt on the validity of the assumption in the kinetic analysis that  $F(W)$  is independent of temperature. The source of this contention is that  $\alpha$ , the degree of degradation inherent in the function, contains a temperature term. It can be shown, however, that  $\alpha$  is independent of heating rate and depends only on the conversion. Under dynamic conditions

$$\alpha = 1 - e^{-\int_0^t k dt}$$

$$\alpha = 1 - e^{-\frac{A}{B} \int_{T_0}^T \frac{E_a}{RT_B} \cdot dT} \quad (10)$$

That  $\alpha$  is independent of  $B$  follows from integral treatments, particularly that in Reference 21. The method is still valid therefore for the random case. The derivation of a pre-exponential factor in the random case may be difficult since the various parameters needed to calculate  $F(W)$  may not be available. Equation 4 is an approximate solution dependent on certain boundary conditions and

may not be applicable to some real cases although the overall random curve is still observed. The normal method of obtaining A from

$$\left( \frac{dC}{dk t} \right)_{\max} = L/e \quad (\text{Reference 5}) \quad (11)$$

and in this treatment,

$$\left[ \log A F(W) \right]_{\max} = \log A + \log \left( \frac{L}{e} \right) \quad (12)$$

must be used cautiously.

### c. Complex Mechanisms

The treatment of two of the more straightforward complex cases was discussed in Reference 6. The first case involved competitive reactions in which the rate curve and thermogram appeared similar to that for a simple reaction except for irregular trends in the maximum rate. The ability of the method to resolve the two reactions depends on how different the individual parameters are. If they have similar orders and activation energies, it is doubtful whether any resolution could be achieved. The second case consisted of two independent reactions, each of which could be observed in thermograms obtained at low heating rates. The corresponding activation energies were obtained at low and high conversions. Only the two methods involving several heating rates showed any success in resolving these cases. In real polymer degradations, the following complex cases have been observed in previous and current work:

a. The thermogram consists of several consecutive steps with distinct plateaus between the decompositions. This case is easily dealt with by treating each step individually as a simple case.

b. The thermogram exhibits overlapping reactions and the DTG curve has several maxima. This could be visualized as Case a. in which the second step commences before the first reaction is complete. This is not strictly analogous to the "independent reaction" discussed in "Complex Mechanisms" since the amount of each reaction may depend on the heating rate. In such a case, a proper analysis may be thwarted although relevant information would still be obtained for the low temperature reaction by studying the initial portion of the weight loss. An example of this type is presented in Section VI.

c. A complex curve somewhat similar to b. has been observed for some aromatic polyesters (Reference 23). For these polymers, the major weight-loss reaction changes smoothly into a slow char-forming reaction which gives the rate curve a long, high temperature tail. Once again, it is predicted that only limited information will be obtained and further discussion must await detailed examination of actual examples.

#### 4. SIGNIFICANCE OF KINETIC PARAMETERS

The influence of experimental variables in programmed thermogravimetry and their effect on the resulting kinetic parameters has been the subject of several reviews (References 2, 8, 19, 24, and 25) and has convinced some authors that the parameters are purely empirical. However, employing careful techniques and strict standardization, many of the sources of error such as weighing errors, diffusion effects, and differences dependent on the physical form of the sample can be minimized or eliminated. The sources of error, which could be considered appropriate to programmed methods and not to isothermal techniques, are heating rate and temperature errors. The latter can be removed by good experimental procedure and, as has been shown previously, the former effect is removed in the ultimate analysis by the method chosen. It is concluded, therefore, that the programmed method used should give information equivalent to that obtained isothermally and it is contended that this information, especially the activation energy, can be meaningful with respect to stability and mechanism. Thus, as in Reference 26, overall activation energies have been related successfully to the energies of individual steps comprising the reaction. A better proof must be to compare the experimental activation energy to that observed in conventional kinetic analysis. This should be feasible when a polymer and its model degrade by exactly similar mechanisms. The field of condensation polymers may contain examples satisfying this condition.

## SECTION III

### EXPERIMENTAL PROCEDURE

#### 1. POLYMER SAMPLES

Descriptions of the methods employed for the preparation and purification of samples are given in the reports which describe in detail the results for those polymers.

#### 2. APPARATUS

The thermobalances used were the Ainsworth Models AV and RV which gave full scale recorder deflections of 100 mg and 10 mg, respectively. In most cases, several deflections of the recorder pen were necessary to follow the complete weight loss of samples.

A sectional diagram of the thermobalance, degradation tube, and furnace is given in Reference 27.

The temperature programmer used was the West Gardsman Model JGB Program Controller which operated a proportioning power supply. The temperature set point was driven by a cam cut to give close to a linear increase in temperature with time. Variation in program rate was effected by changing gears in the motor to cam gear train. Some of the approximate program rates selectable were 75, 90, 150, 280, and 450° per hour but the actual program rates were calculated for each run from the temperature-time data.

#### 3. TEMPERATURE MEASUREMENT

The measurement of the actual temperature of a material undergoing weight loss presents many difficulties. In theory, an ideal method for measuring the temperature would be to surround a thermocouple bead completely with the sample and measure the thermocouple millivolt output. In practice, difficulties arise especially if complete loss of material takes place during degradation. In this case, the thermocouple bead becomes more and more exposed to the heat source as weight loss occurs. Further, it may not be safe to assume a correct temperature will be determined even when the sensor is completely surrounded. This will be dependent upon the spectral characteristics of the sample and the heating method employed (UV or IR).



Another difficulty is involved in the simultaneous determination of weight and temperature. Torsion of wires from the thermocouple to a stationary support will alter the mass reading or may cause noise in the weight record. Methods differing in complexity have been devised to overcome these defects but none is entirely satisfactory (References 19 and 28).

For this work, it was decided to measure temperatures by placing a thermocouple in a thermowell as close to the sample as possible. For several of the polymers, a series of calibration degradations was run. Sample temperature, measured by a thermocouple in direct contact with the polymer, was recorded and corrections to the thermowell temperatures were obtained.

In most cases, the temperature correction,  $\Delta T$ , was of the form

$$\Delta T = C + A\beta$$

A and C are constant

$\beta$  is the heating rate

The temperature corrections were usually in the range of 5 to 15°C. Similar lags have previously been reported (Reference 24).

In the range of temperatures over which weight loss occurs, severe temperature lags may occur (Reference 25) since large quantities of heat are called for during an endothermic process.

It is realized that temperatures measured in this work are only approximate but it is felt that by standardizing conditions (sample size, crucible and furnace geometry, etc.) and making the corrections described, errors are minimized. It is hoped eventually to be able to recalculate this data making corrections for the lag during the endothermic weight loss. This must await the relevant experimental data.

#### 4. PROCEDURE

The sample (usually 100 mg) was weighed into a small quartz crucible which was then suspended in a quartz degradation tube by a fine nichrome chain connected to the balance beam. A counterbalance was applied to the opposite side of the beam making sure that weights at least equal to the expected weight change were suspended on the beam. After the apparatus had been pumped down to a pressure below 0.1 micron of mercury, the furnace which surrounds the degradation tube and the programmer were switched on. After the weight change had occurred, programming was continued until a good final weight base line was recorded. From the thermogram which recorded both weight and temperature as a function of time, the rates of weight loss as a function of the instantaneous percent weight loss were computed (Section IV). In any cases in which a steady final weight line could not be obtained (e.g., for some aromatic polyamides and polyesters), rates were based on the initial sample weight instead of on the total weight loss.

Occasionally slight initial weight losses were noticed due to removal of solvents or water from the polymers. In these cases, data were taken from the thermogram after the weight line was again level.

In an attempt to reduce procedural errors, the experimental procedure and apparatus were standardized as far as possible (e.g., furnace, method of temperature measurement, sample size, crucible geometry).

Extremely useful information on experimental methods and apparatus used in thermogravimetry is given in Reference 25.

## SECTION IV

### COMPUTER HANDLING OF THERMOGRAVIMETRIC ANALYSIS DATA

This section is devoted to the treatment of TGA data using Friedman's method which is discussed at length in Section II. There is some similarity to the treatment of isothermal thermogravimetry data (Reference 35). Despite the possible repetition, this section describes all aspects of the handling of programmed thermogravimetry data. The first of this section is concerned with the determination of the rates of weight loss and the second portion describes the evaluation of the parameters involved in Equation 9.

#### 1. COMPUTATION OF RATE OF WEIGHT LOSS

In Section III the experimental procedure is described. Figure 2 shows a typical recorder trace from the thermobalance. The two curves represent temperature (measured by a Chromel/Alumel thermocouple located in a thermowell close to the sample container) and the sample weight (measured electronically by determining changes in the resonant frequency of a transducer caused by deflection of the balance beam). The pen excursions are linearly dependent upon temperature and weight, full scale deflections corresponding to 500 or 1000°C and 10 mg or 100 mg weight change.

Obviously the two pens cannot travel on the same line perpendicular to the time axis. A small correction has to be made to data read from the same line to ensure that pairs of weights and temperature data represent conditions at the same time.

Methods are available for automatically converting signals from measuring equipment to digital form for computer processing, but such methods were not on hand for this work. Thus it was necessary to obtain the recorder traces and to take data from the two curves either using a mechanical graph reader or manually. In the latter method, the chart was taped to a board and scales graduated in suitable increments (20th or 32nd of an inch) taped to both sides of

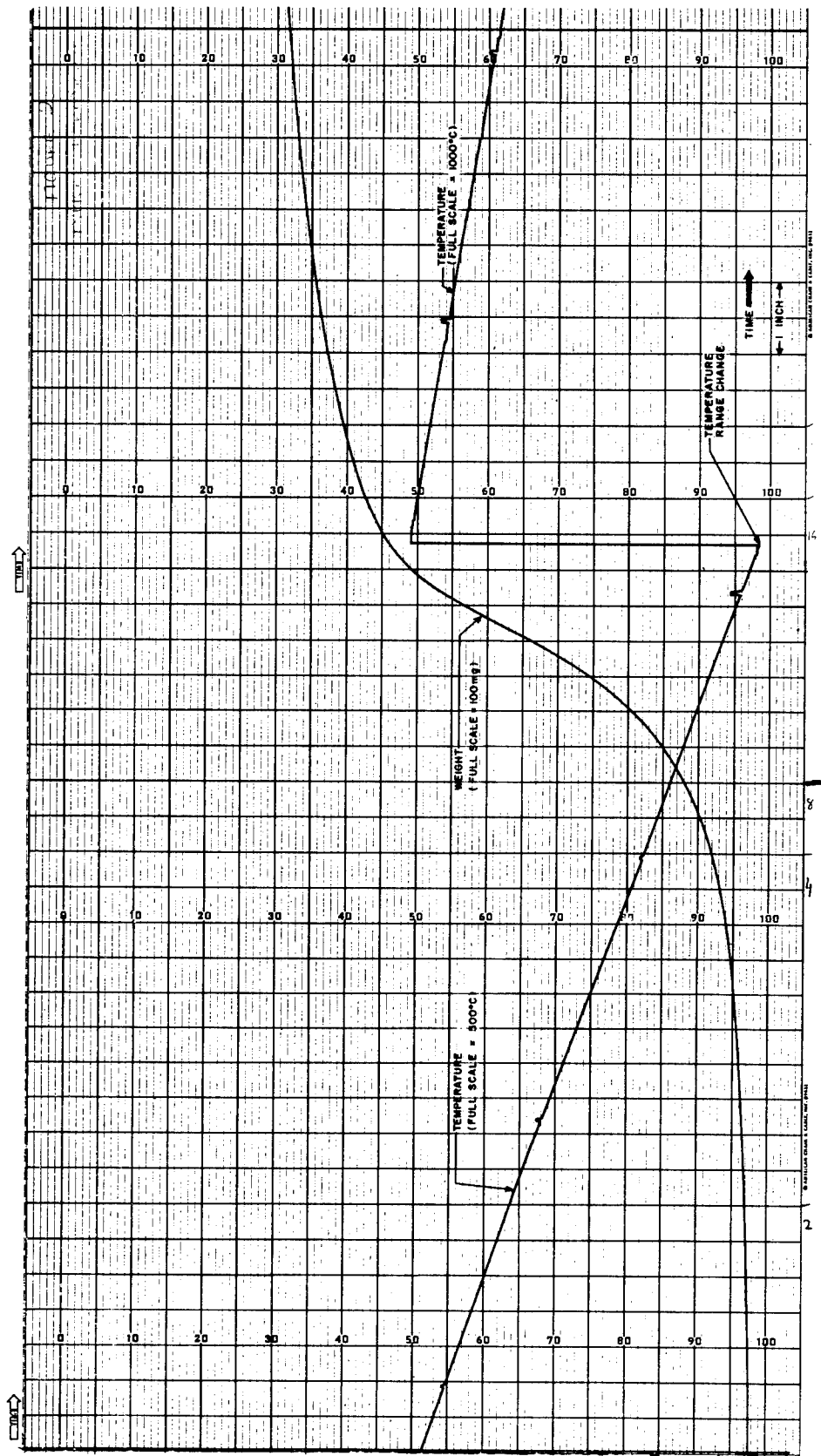


Figure 2. Typical Thermogram

AFML-TR-68-181  
Part II

the chart parallel to the time axis. A ruler was then moved along the time axis and corresponding weight and temperature data recorded at 200 to 300 positions. In order to simplify data gathering, elapsed inches of chart were recorded and time regenerated during the machine calculations using the chart speed (in inches per minute). The zero time data is taken from the curve at some suitable position prior to significant weight loss.

The first card identifies the deck of cards that follows. The information and the columns in which it is punched is shown in Table III.

TABLE III  
IDENTIFICATION CARD

COLUMNS	CONTENTS
1 - 8	Any identification, name, etc.
9 - 12	Run number (e.g., O4P)
13 - 14	Blanks
15 - 22	Date
23 - 24	Blanks
25 - 45	Alphabetic information, polymer name, etc
46 - 52	Chart speed in inches per minute
53 - 54	Blanks
55 - 59	Pen offset in inches
60 - 62	Inches between first and last data
63 - 70	Blanks
71 - 73	Temperature at initial time reading
74 - 76	Blanks
77 - 79	Temperature at final time reading

## Part II

Following the identification card is the data deck. The data cards are punched as shown in Table IV. A typical input card deck is reproduced in Appendix I.

TABLE IV  
CONTENTS OF DATA CARDS

COLUMNS	CONTENTS
1 - 13	Identification information, name, etc.
14	An index, LBJ, to signal the end of a deck
15 - 17	Blanks
18 - 22	Time in inches
23 - 28	Weight
29 - 32	Temperature
33	Blank
34 - 38	Time in inches
39 - 44	Weight
45 - 48	Temperature
49	Blank
50 - 54	Time in inches
55 - 60	Weight
61 - 64	Temperature
65	Blank
66 - 70	Time in inches
71 - 76	Weight
77 - 80	Temperature

Using the input data, the computer assembles a matrix of time, weight, and temperature data which is then scanned to find the next weight after a 1% weight loss. A number of pairs of weight and time data either side of this point is then fitted to a quadratic (using PLSQ least squares curve fit subroutine). The quadratic is then solved for the time taken for an exact 1% weight loss to occur. These calculations are repeated for all integral percent weight losses up to 99.

Time and temperature data are fitted to a polynomial using the PLSQ subroutine. A single high order polynomial is used to fit all the temperature-time data whereas a quadratic is used to fit short sections of the weight-time data. These two different methods were chosen because a quadratic may easily be solved whereas higher orders may not. Only substitution into the time-temperature polynomial is needed here so high orders may be used to get a better fit of the data. The weight-time curve fit, however, had to be solved to interpolate time values; as a quadratic fit was dictated, the best fit was achieved by using a relatively small number of curve fit data.

After the input data has been compared with results calculated from the fitted curves, the spurious input is replaced by fitted values and the curve fits recalculated. The rate of weight loss is then calculated for each percent weight loss and the average heating rate computed. A schematic representation of this rate program is given in Figure 3, and the complete program is reproduced in Appendix II.

Finally the results are printed out in tabular form together with graphs representing the variations of rate of weight loss with percent weight loss, weight with time, and temperature derivative with time. Results are also punched on to computer cards for further processing. A typical punched card output deck is shown in Appendix III and examples of pointout data is given in Appendix V.

## 2. COMPUTATION OF ARRHENIUS PARAMETERS

Friedman's method for calculating activation energy, etc., which is described fully in Section II, requires the comparison of weight-loss rates obtained from a number of thermogravimetric analyses carried out at differing rates of temperature increase. Comparison is made between rates of weight loss at identical extents of weight loss, and activation energy may then be calculated from the slope of the curve of  $\log$  (rate of weight loss) against reciprocal of the absolute temperature. The lower the heating rate, the lower the temperature will be for a given weight loss.

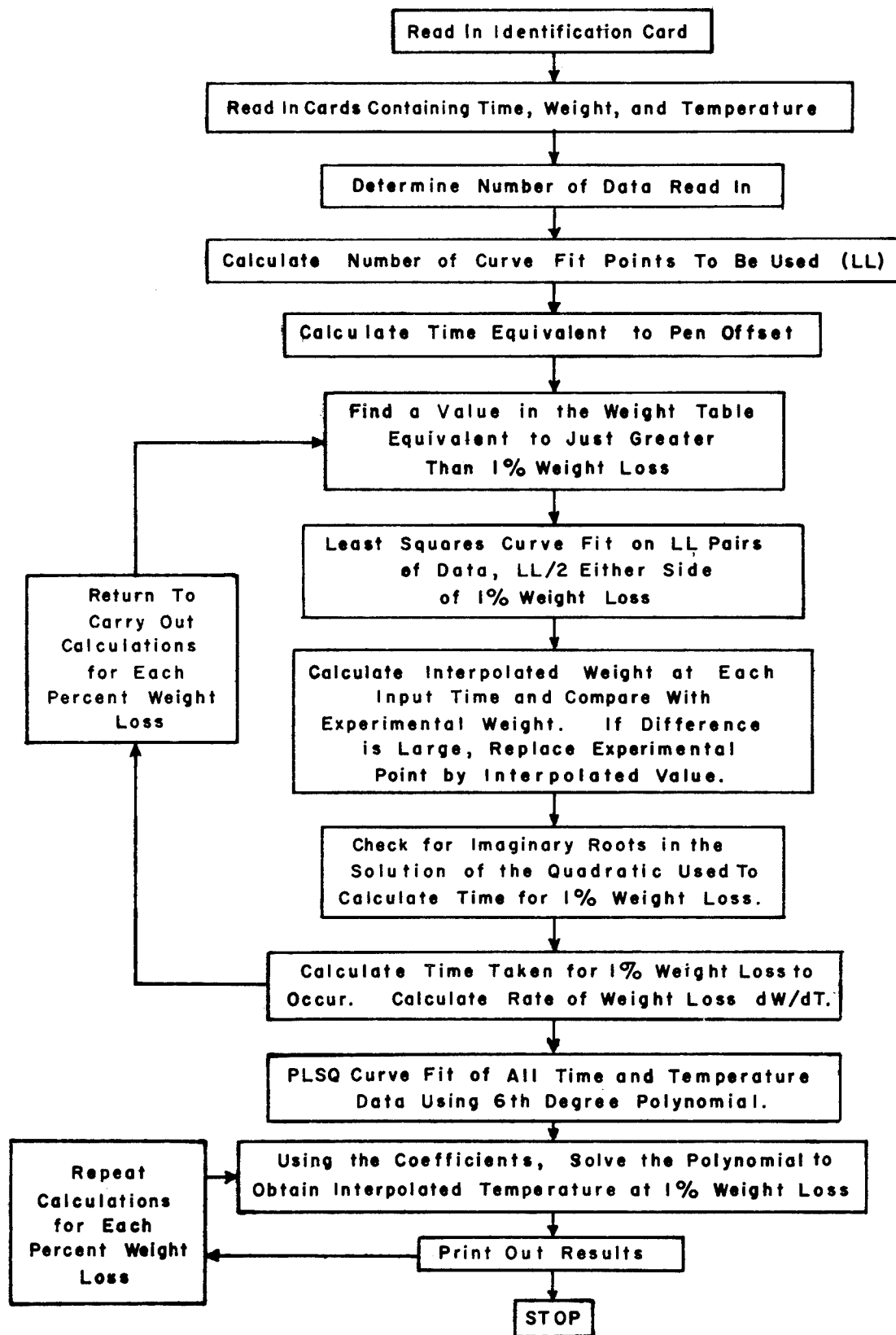


Figure 3. Schematic Representation of Rate of Weight Loss Calculations



The output punched cards from the rate program contain both rate of weight loss and temperature for each percent weight loss so the program merely selects corresponding data from each experiment and carries out a least squares straight line fit of the log (rate of weight loss) and  $1/T$  data. Both the slope and intercept of the best line are computed.  $\log A F(W)$  values are then calculated using an average value for the activation energy. The range of weight loss over which this average is computed is usually chosen to omit very low and high conversions. A discussion of the effects of changes in activation energy with conversion is in Section II.

Figure 4 shows a schematic representation of Arrhenius parameter calculations, and in Appendix IV the complete Arrhenius program is reproduced. Typical results from all these calculations are presented and discussed in Section V.

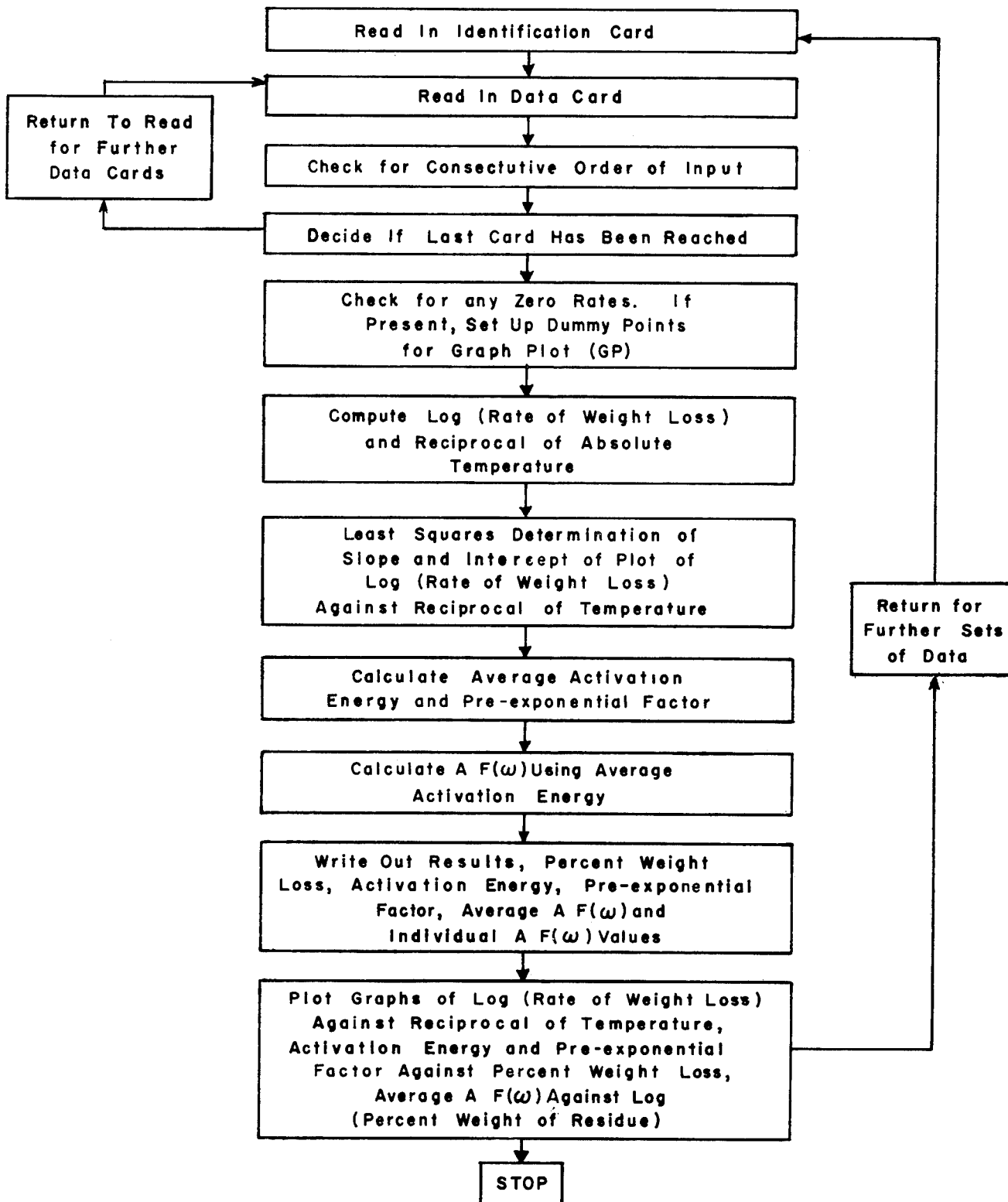


Figure 4. Schematic Representation of Arrhenius Parameter Calculations

## SECTION V

### WEIGHT LOSS OF POLY(TETRAFLUOROETHYLENE)

To validate the procedure for the determination of activation energy and order of reaction which is described in Section II, results obtained by this method were compared with those previously published for the degradation of poly(tetrafluoroethylene), Teflon. This particular compound was chosen for its relative lack of complications and for the availability of published information.

Madorsky and co-workers (Reference 29) measured the weight of samples of Teflon maintained at fixed temperatures. Plots of the rate of weight loss against the percent volatilization were linear between about 20 and 80% volatilization showing the degradation to be a first order process. Their kinetic data could be summarized by the following equation

$$k_1 = 4.7 \times 10^{18} e^{-80,500/RT} \text{ sec}^{-1}$$

$k_1$  = first order rate constant

R = gas constant

T = absolute temperature

A mechanism for degradation involving thermal, weak link, or end initiation followed by unzipping of the free radicals produced was postulated.

Wall and Michaelson (Reference 30) confirmed these observations but suggested that a zero order dependence of the rate of weight loss on sample weight was observable below about 480°C. They presented data which showed that at 460°C under nitrogen the weight loss of Teflon is a linear function of time up to about 40% weight loss.

Anderson (Reference 31) analyzed Teflon thermogravimetry data by the method of Freeman and Carroll (Reference 11) and found the degradation, in vacuum, to be first order between 450 and 550°C with an activation energy of 75  $\pm$  4 kcal/mole.

Reich and co-workers (Reference 13) analyzed Teflon weight-loss data using the method of Anderson and Freeman (Reference 12) previously discussed. They obtained activation energies varying between 69 and 74 kcal/mole, the average being 72 kcal/mole.

Lee and co-workers (Reference 32) presented information obtained using heating rates between 300 and 1200°C per hour. It will be shown here that such high heating rates are likely to result in large uncertainties in the temperature measurement with consequent curvature of activation energy plots. However they quote  $E_a$  between 60 and 69 kcal/mole and orders of reaction between 0.7 and 0.85 depending on the method of plotting employed.

Carroll and Manche (Reference 33) re-examined Madorsky's data and determined the activation energy as a function of the conversion and showed that between 10 and 80% weight loss the activation energy decreases from 80 to about 46 kcal/mole. The decrease of  $E_a$  with increasing conversion was apparent for both the programmed temperature increase and for the isothermal weight loss of Teflon in vacuum. The reaction was said to be zero order.

Section II gives a detailed discussion of the various techniques which have been used for calculating kinetic parameters from weight-loss data. Our conclusions are that each method has serious shortcomings. We, therefore, consider that the data of Madorsky (Reference 29) which was obtained isothermally should be the most reliable for comparison with the results of our investigation.

As a check on the present differential method for the determination of  $E_a$  and order of reaction, a series of programmed temperature increase, vacuum weight loss, experiments on 100 mg samples of Teflon was carried out using heating rates between 45 and 450° per hour. The polymer used was Du Pont Teflon molding powder Composition 6 in the form of fine granules.

The first runs which were carried out at the higher heating rates gave very high rates of weight loss (~10% per minute). With such high rates of reaction, considerable temperature lags might be expected so measurements were also made using very low heating rates (below 150° per hour).

Figure 5 is a plot of  $\log$  (rate of weight loss) against the reciprocal of the absolute temperature for 50% conversion. Plots for other conversions were similar to this one. It is evident that a straight line cannot be drawn to represent the data over the whole temperature range. However, the runs carried out at  $150^\circ$  per hour and lower heating rates do show a linear dependence of  $\log$  (rate of weight loss) on  $1/T$ . The slope of the line drawn through only these four points gives an activation energy of 69.3 kcal/mole. A case could be made for considering only the three lowest heating rates. The derived activation energy would then be increased.

It is probable that the curvature of the Arrhenius plot when the higher heating rates are used is due to the large thermal lags when the rates of weight loss are large. In the hope of bringing these results into line, an attempt will be made to correct for these lags by direct sample measurement.

The computer printout for the rates of weight loss for one of the Teflon experiments is given in Appendix V and Appendix VI shows the rates of weight loss at each 1% conversion for the four lowest heating rate runs. Appendix VII is the computer printout for the activation energy calculations based upon all the rates quoted in Appendix VI. Figure 5 contains all the 50% data from Appendix VI as well as data obtained using higher heating rates.

#### 1. VARIATION OF ACTIVATION ENERGY WITH CONVERSION

Figure 6 shows a plot of activation energy as a function of weight loss, the data being taken from Appendix VII. Between 4 and 99% weight loss, activation energy varies between about 62 and 83 kcal/mole. The average value of 69.34 kcal/mole between 10 and 80% weight loss has been used to calculate  $\log A F(W)$  values used in one of the curves in Figure 7. Careful inspection of the activation energy data reveals an approximately constant value, average = 63.98 kcal/mole, between 10 and 50% weight loss. At greater conversions,  $E_a$  increases slowly to a maximum which is maintained between 65 and 80% weight loss.

It has been reported that Teflon undergoes a change in physical properties above 50% weight loss. In Reference 30 it is claimed that the polymer melts

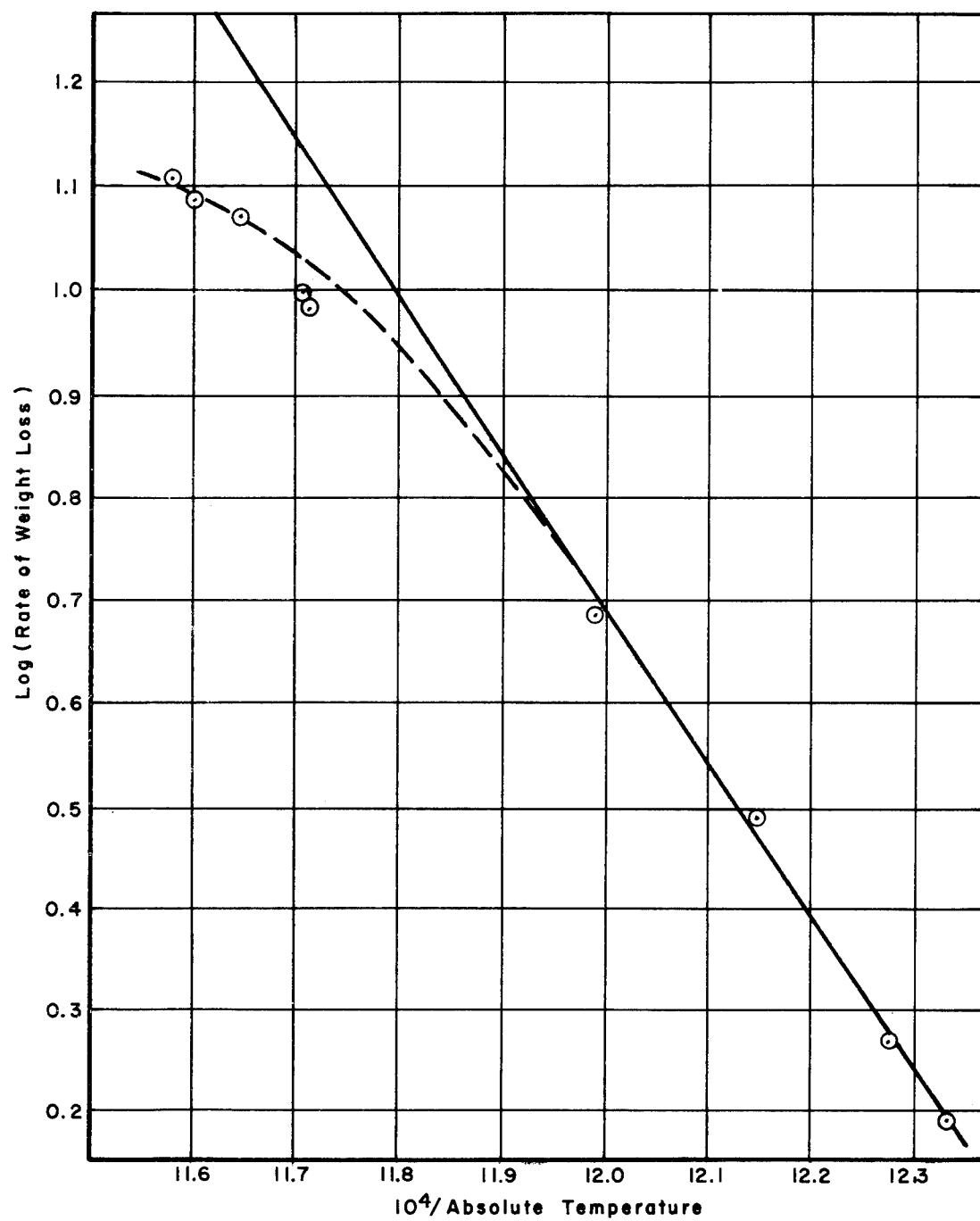


Figure 5. Arrhenius Plot for Degradation of Teflon at 50% Weight Loss

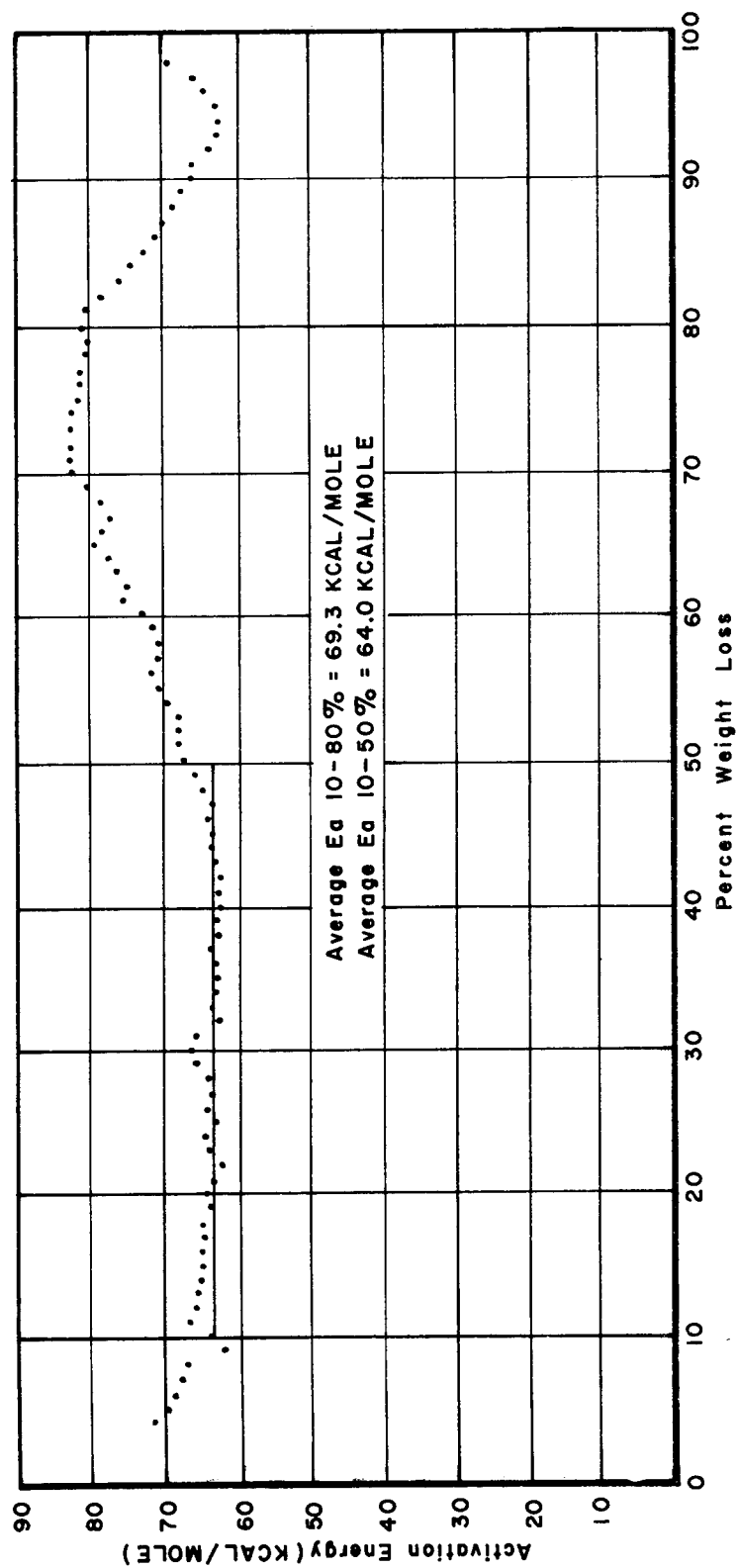


Figure 6. Variation of Activation Energy with Conversion for the Weight Loss of Teflon

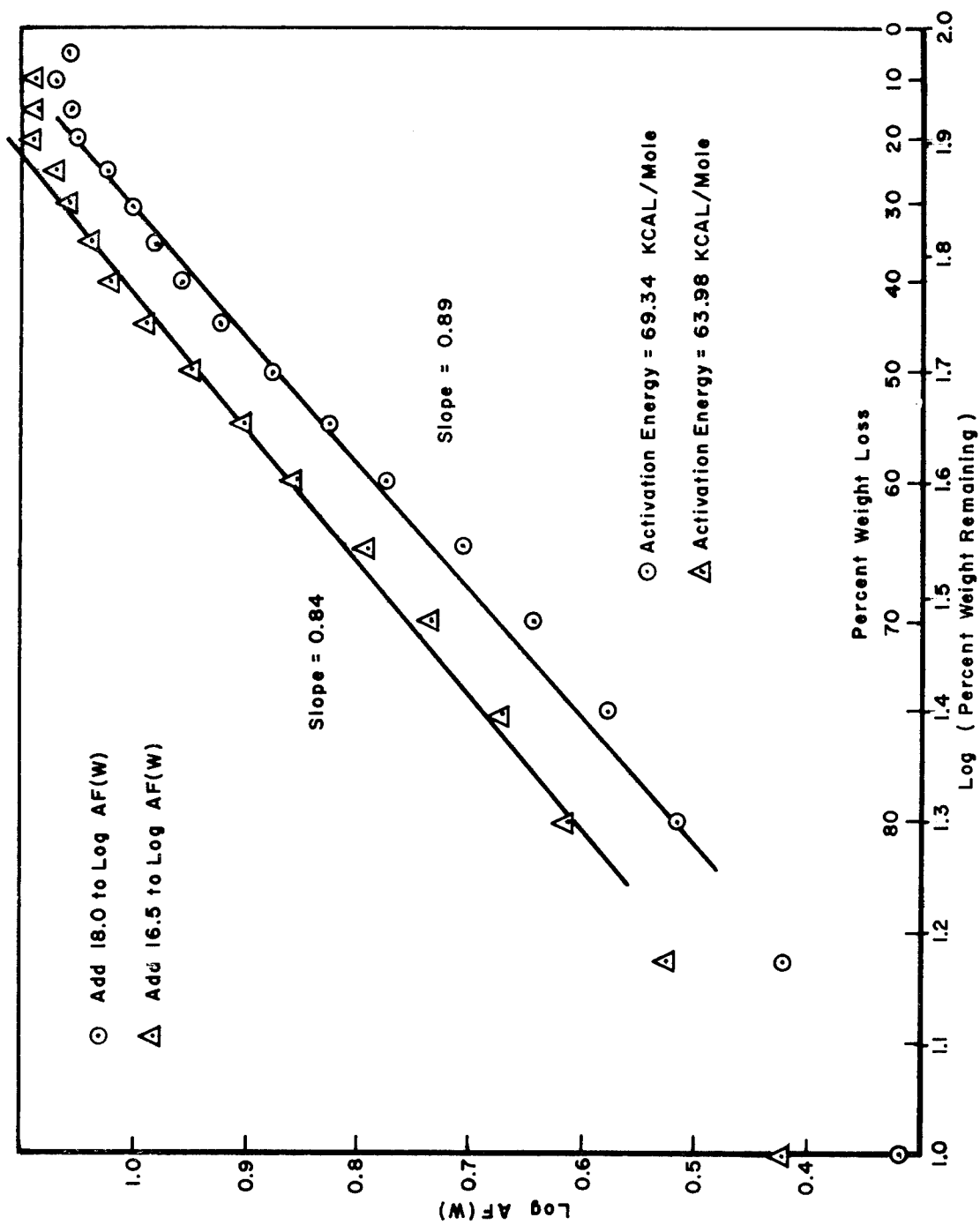


Figure 7. Log A F(W) Curves for Teflon Degradation



at this conversion. There may be some correlation between this phenomenon and the change in the activation energy curve at the same conversion.

## 2. ORDER OF REACTION

Figure 7 also shows the  $\log A F(W)$  obtained using the activation energy average for the 10 to 50% weight loss (i.e., 63.98 kcal/mole). The straight lines drawn which represent the 20 to 80% weight loss data fairly well have slopes of 0.84 and 0.89, and only slight maxima in the  $\log A F(W)$  curves are apparent at very low conversions. Thus the weight-loss process obeys approximately first order kinetics. Other lines having differing slopes may be drawn through points representing more limited weight loss ranges but it would be unwise to assign real significance to such slopes.

## 3. PRE-EXPONENTIAL FACTOR

The extrapolated value of  $\log A F(W)$  at zero percent weight loss is a measure of the pre-exponential factor ( $A$ ). Using the low  $E_a$  value,  $\log A = 15.7$ , with the high  $E_a$ ,  $\log A = 17.1$ . (Note: Since weight losses used here are in percent,  $\log 100$  has been subtracted from each intercept.)

## 4. DISCUSSION

The data presented here is in fair agreement with some of the published information. The 10 to 80% average activation energy is about 10 kcal/mole lower than Madorsky's value. The change in  $E_a$  with conversion does not agree with the drop from 80 to 46 kcal/mole calculated by Carroll and Manche (Reference 33). It is, however, more reasonable to expect the increase in  $E_a$  with conversion, as we find, then to expect a large drop in  $E_a$ .

If the degradation involves unzipping with a long kinetic chain length throughout the total weight loss, a first order rate dependency would be indicated, and no changes in molecular weight of the residue would occur. It has been shown (Reference 34) that, at 500°C, tetrafluoroethylene is the major volatile product of degradation (95%) but small amounts of  $CF_4$  and  $C_3F_6$  are also produced. At higher temperatures, the yield of tetrafluoroethylene is reduced, other products being produced by termination of short kinetic chain length unzipping processes. If the kinetic chain length is shorter than the degree

of polymerization, a change in molecular weight of the residue would take place during weight loss with consequent complication of the degradation mechanism.

It is felt that the method described here for the determination of kinetic parameters involved in thermogravimetry gives adequate agreement with literature data for Teflon to justify its application to other systems. The kinetics of degradation of polymers which obey more complicated laws are discussed in Section VI.

## SECTION VI

### DEGRADATION OF OTHER POLYMERS

In this section, representative examples of results obtained during thermal degradation of polycondensates are discussed. These examples have been chosen to show several types of  $\log A F(W)$  curves which are derived from weight-loss data using the computational methods described in Section IV.

#### 1. POLY (1,4- PHENYLENE SEBACATE)

Figure 8 shows how the rate of weight loss for this polymer varies with the extent of conversion. That the mechanism of the degradation of this polymer is more complex than that for poly(tetrafluoroethylene) is shown by the fact that the curve of rate of weight loss against percent weight loss exhibits two distinct maxima, one at about 45% and the second at about 90% of the overall weight loss. Since separation of the maxima is apparent, the activation energies of the individual processes must differ appreciably. The greater the energy difference, the better will be the resolution of the rates of each process.

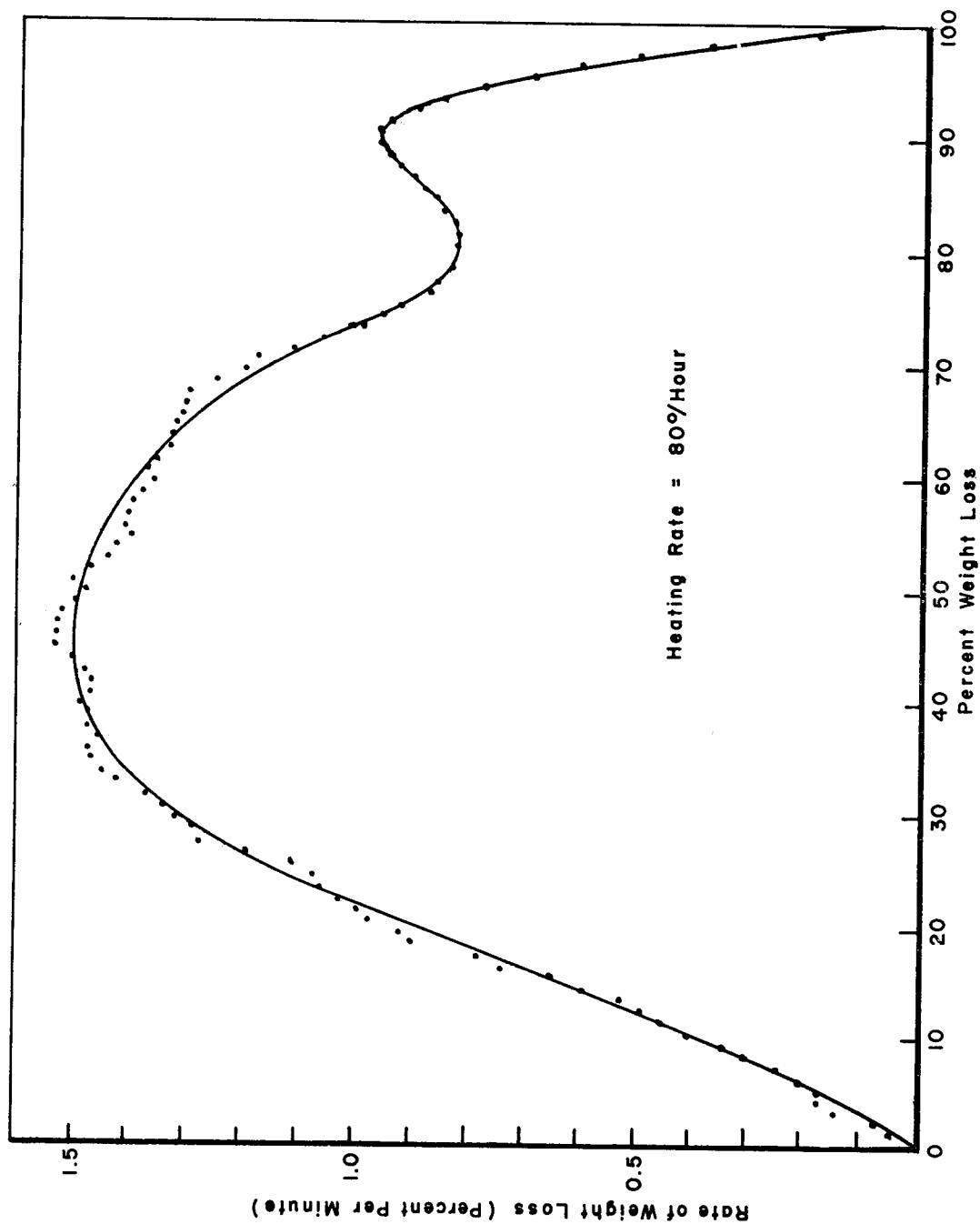


Figure 8. Rate of Weight Loss of Poly(1,4-phenylene sebacate) as a Function of Weight Loss

Figure 9 shows that the activation energy does indeed vary during the degradation of poly(1,4-phenylene sebacate). In the early stages of degradation (Line A),  $E_a$  is about 30 kcal/mole and a gradual rise takes place until  $E_a$  is close to 60 kcal/mole during the final 20% weight loss (Line B).

The curve of  $\log A F(W)$  against  $\log$  (residue weight-percent), produced when the overall average  $E_a$  of 36.1 kcal/mole is used, is shown as Curve III in Figure 10. A change in the slope of this curve is apparent at conversions exceeding about 70% showing the change in mechanism brought about by the commencement of the second reaction. As explained in Section II, an erroneously high slope would be derived from this curve since this type of plot should be based on the weight loss during a single component reaction, here the weight-loss data is based on the sum of the two component reactions.

In order to separate the contributions due to each of these two processes, it is necessary to go back to the original curve of rate of weight loss as a function of overall percent conversion (Figure 8) or the curve of rate of weight loss against temperature (Figure 11). By careful inspection and judicious use of curve drawing techniques, it is possible to resolve the two peaks, from either curve, into the pure components. Overlap of the two reactions occurs between about 45 and 80% of the total weight loss. When a separation has been made, calculations of  $\log A F(W)$  for each component may be made using the relevant conversions. The required activation energies are found from the approximately linear parts of the  $E_a$  against weight-loss curve (Lines A and B in Figure 9).

Figure 10 shows the results of such a resolution of a complex weight-loss process. Curve I is the  $\log A F(W)$  plot for Component Reaction I. This process is probably random, the low conversion rise in this curve probably being due to an early low activation energy weight-loss process. Curve II represents Component Reaction II. The drop in the curve at low conversion may not be significant since this is the region of maximum overlap with Reaction I. The slope of the curve at higher conversions shows the reaction obeys either first order or random kinetics.

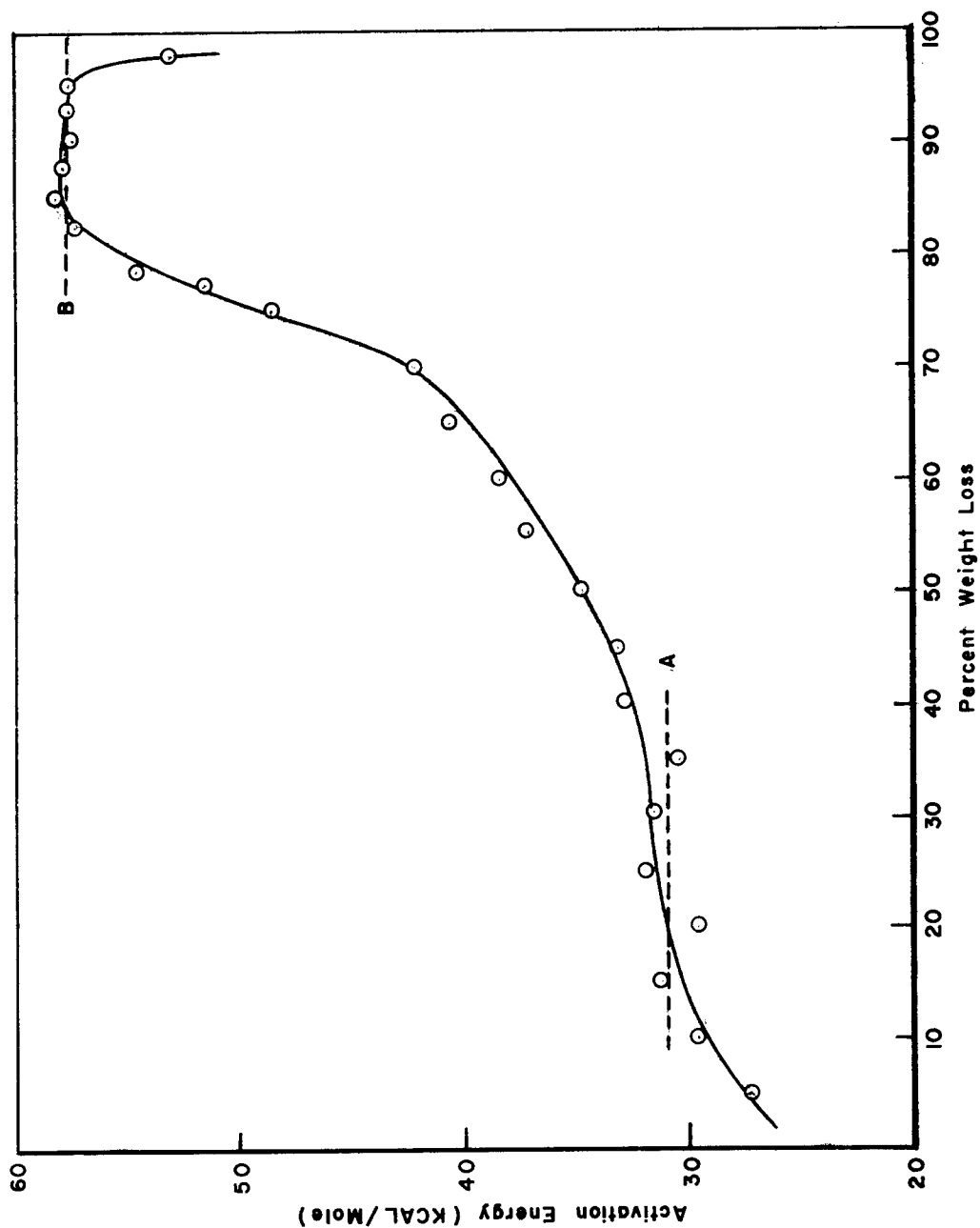


Figure 9. Activation Energy as a Function of Weight Loss for Degradation of Poly(1,4-phenylene sebacate)

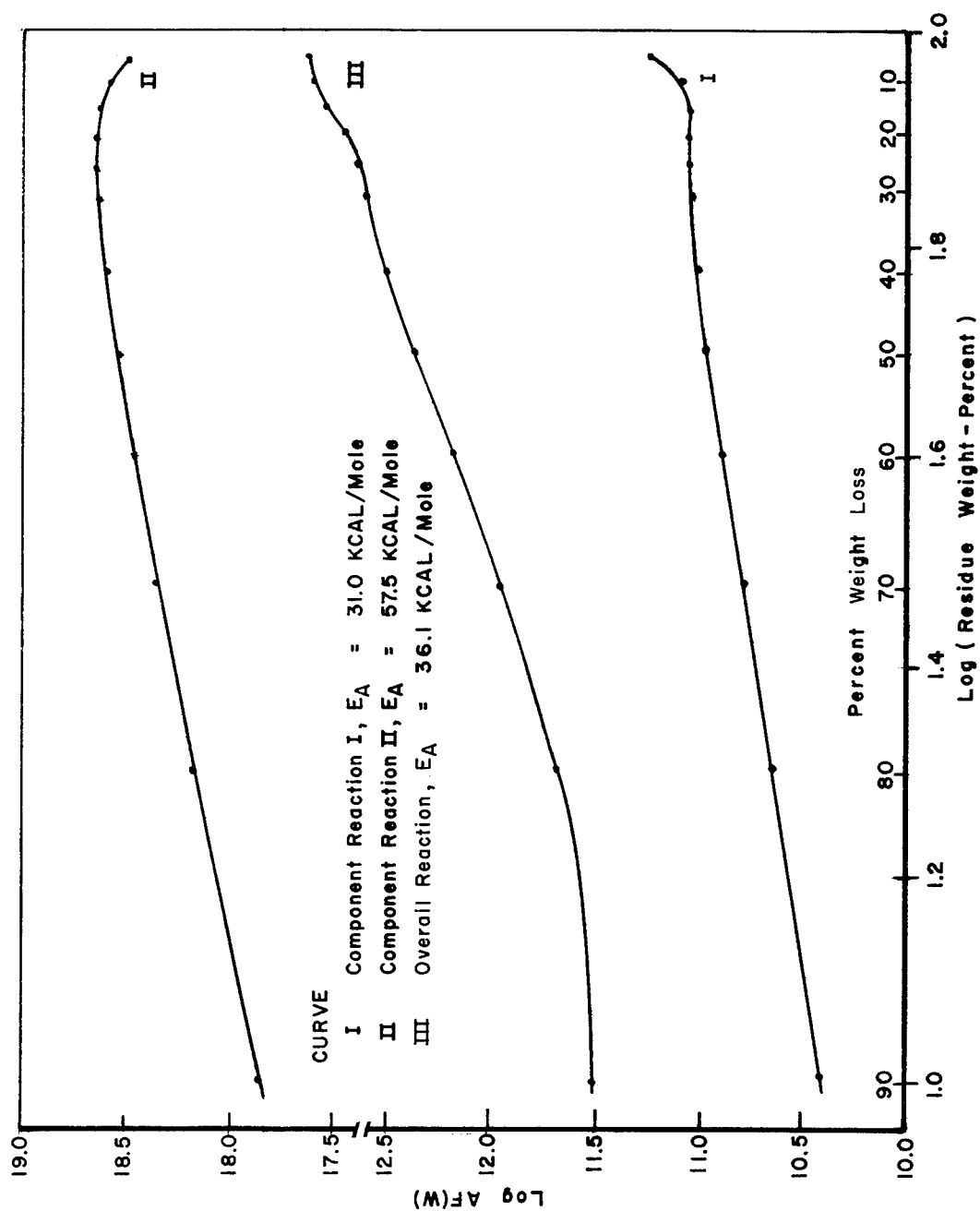


Figure 10. Log A F(W) Curves for Overall and Component Reactions in the Degradation of Poly(1,4-phenylene sebacate)

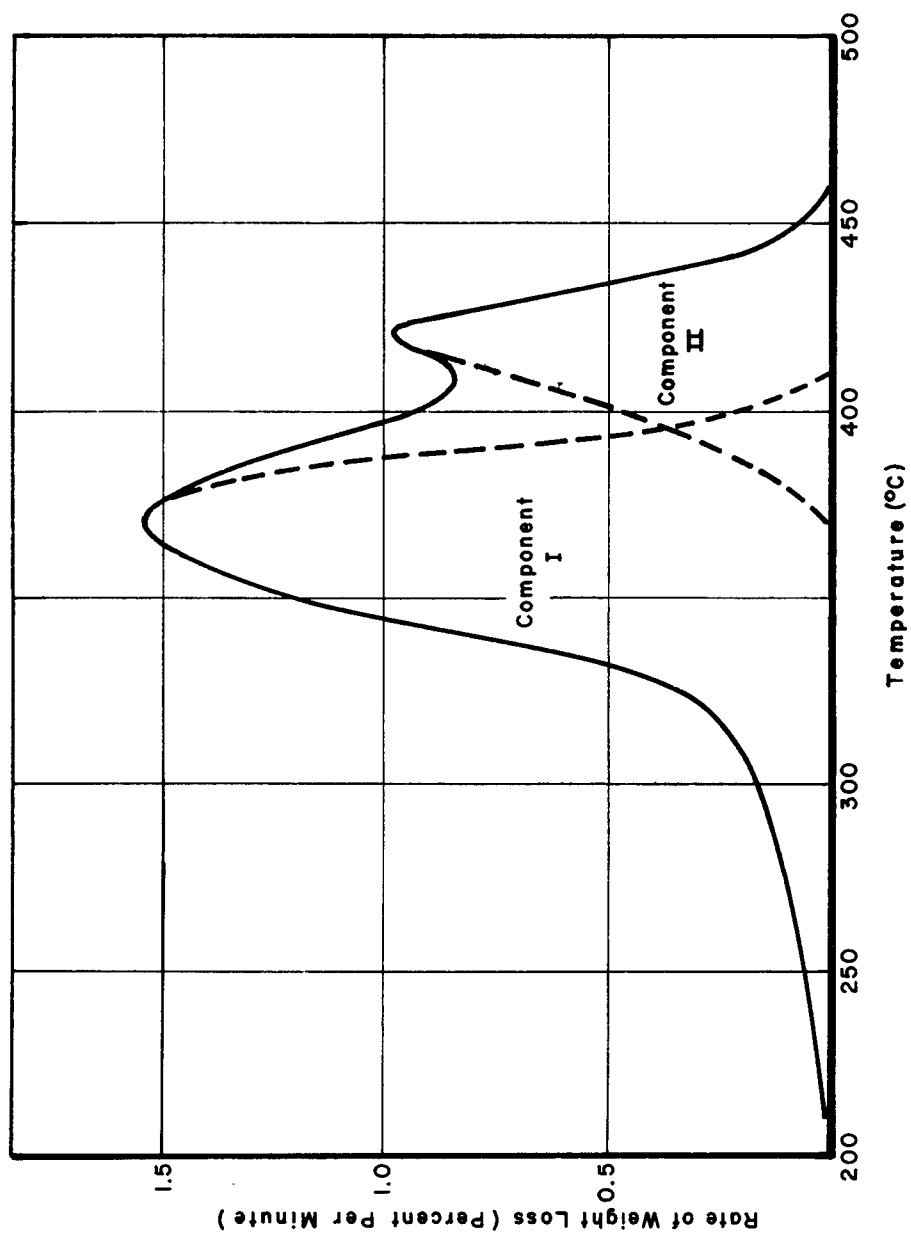


Figure 11. Separation of Rate of Weight Loss/Temperature Curves

Thus it can be seen that it is possible to separate to some extent the components of a complex weight-loss process. However, where overlap occurs there is some doubt about the rates of the individual weight losses. This doubt is reflected in the inability to assign real significance to the part of the  $\log A F(W)$  curve which includes considerable overlap of reactions.

A case could be made from the data shown in Figure 8 that another component may be present in the range 60 to 70% weight loss but even if real it would be virtually impossible to achieve its resolution.

A similar treatment of the same data is given in Reference 23.

## 2. POLY(HEXAMETHYLENE SEBACAMIDE), NYLON 6.10

Unlike many aromatic polyamides (Reference 40), nylon 6.10 degrades completely leaving no appreciable residue. The maximum rate of weight loss occurs at about 60% weight loss.

Figure 12 shows the variation of activation energy with the extent of weight loss determined from programmed thermogravimetry data. The activation energy rises rapidly during the first 10% weight loss and then remains in the region of 57 kcal/mole for the remainder of the weight-loss process. The early rise in  $E_a$  can probably be attributed to the removal of absorbed water from the polymer or distillation of low molecular weight volatiles. Using an activation energy of 57.2 kcal/mole, the  $\log A F(W)$  curve shown in Figure 13 has been constructed. The 20 to 90% weight-loss data is represented by a good straight line having a slope of 1.02 indicative of a random or first order decomposition mechanism. The downward curvature of the line at low conversions tends to indicate a random process is operative especially as the maximum occurs close to 25% weight loss (Reference 5). Other workers have concluded that the same mechanism describes the degradation of other polyamides but a possible ionic hydrolysis process may occur simultaneously (Reference 38).

Several other aliphatic polymers have been studied and found to yield similar  $\log A F(W)$  curves and mechanistic interpretations. The degradation of several aliphatic polyesters and polyamides is discussed in References 36 and 39.



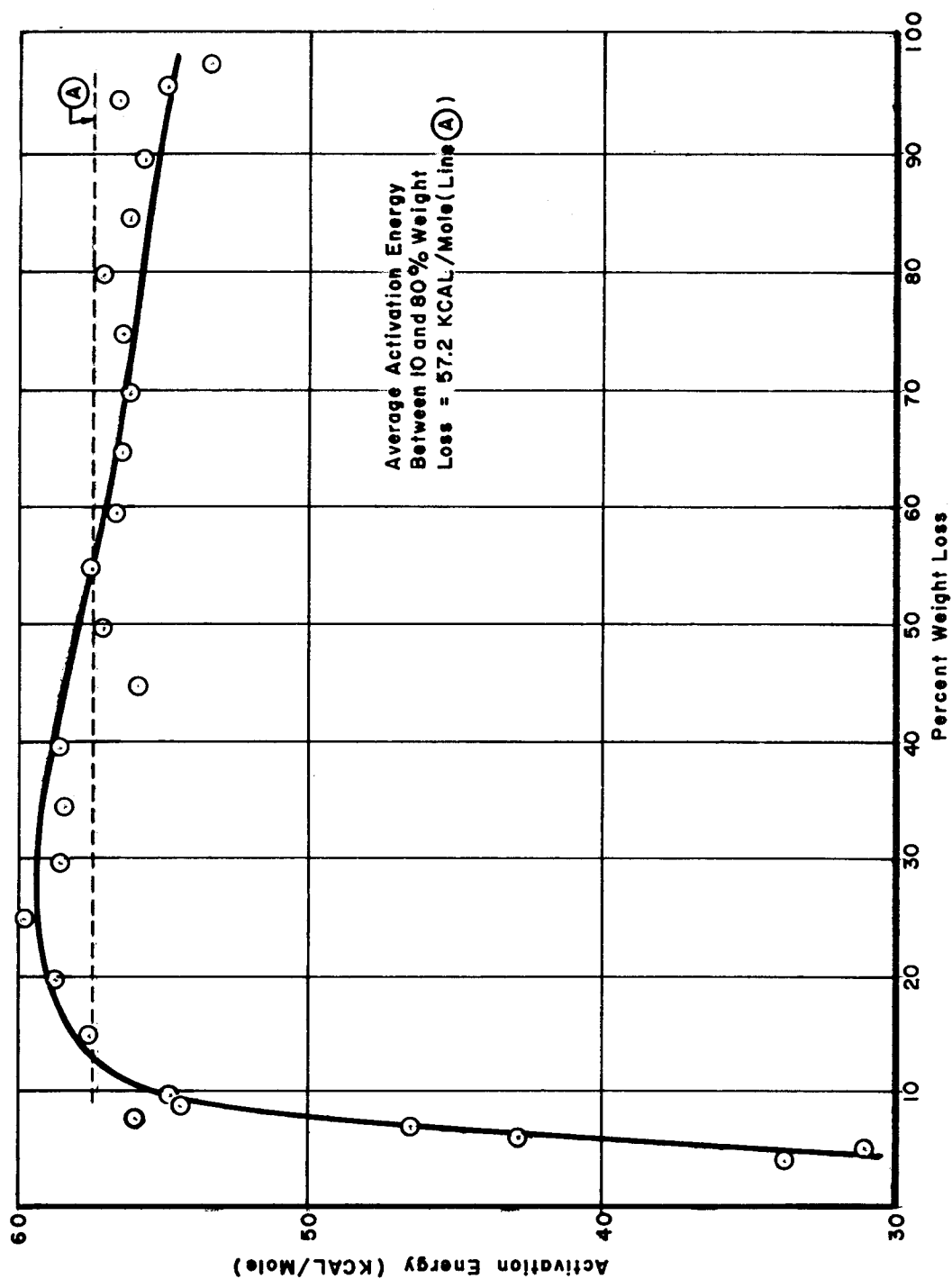


Figure 12. Activation Energy for Weight Loss of Nylon 6.10

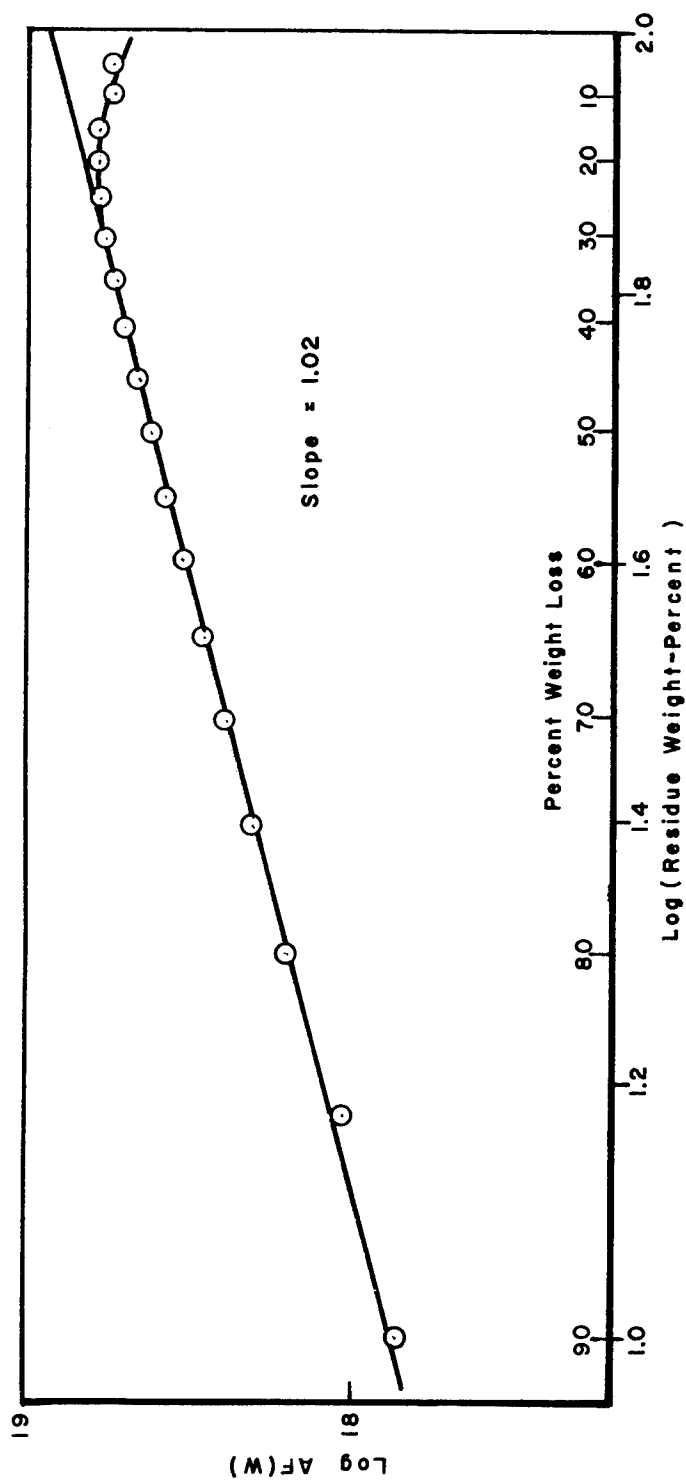


Figure 13. Log A F(W) Curve for the Weight Loss of Nylon 6,10

## SECTION VII

### CONCLUSIONS

The method of Friedman has been shown to be applicable to a wide variety of polymer degradations. It can detect a single first order weight loss, one where random decomposition is suspected (as noted by a maximum in the rate law curve) and can provide some resolution of a weight-loss curve showing more than one rate maximum. It is our conclusion that only through the use of several thermograms at different heating rates can this information be obtained reliably.

## REFERENCES

1. N. Grassie, "Chemical Reactions of Polymers," edited by E. M. Fettes, Interscience, New York-London-Sidney, 1964, pp 565-644.
2. C. D. Doyle, Techniques and Methods of Polymer Evaluation, Vol. 1, edited by P. E. Slade and L. T. Jenkins, Marcel Dekker, Inc., New York, 1966, pp 113-216.
3. J. H. Flynn and L. A. Wall, Rubber Chem. & Technol., 35(5), 1962, p 1157.
4. R. Simha, L. A. Wall, and P. Blatz, J. Polymer Sci., V(5), 1950, p 615.
5. R. Simha and L. A. Wall, J. Phys. Chem., 56, 1952, p 707.
6. J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Standards, 70A(6), 1966, p 487.
7. C. D. Doyle, J. Appl. Polymer Sci., V(15), 1961, p 285.
8. A. W. Coats and J. P. Redfern, Analyst 88, 1963, p 906.
9. C. B. Murphy, Analyt. Chem., 36(5), 1964, p 347.
10. R. M. Fuoss, I. O. Salyer, and H. S. Wilson, J. Polymer Sci., 2A, 1964, p 3147.
11. E. S. Freeman and B. Carroll, J. Phys. Chem., 62, 1958, p 394.
12. D. A. Anderson and E. S. Freeman, J. Polymer Sci., 54, 1961, p 253.
13. L. Reich, H. T. Lee, and D. W. Levi, J. Polymer Sci., B1, 1963, p 535.
14. P. K. Chatterjee, J. Polymer Sci., 3A, 1965, p 4253.
15. H. L. Friedman, J. Polymer Sci., 6C, 1965, p 183.
16. A. W. Coats and J. P. Redfern, Polymer Letters, 3, 1965, p 917.
17. L. Reich and D. W. Levi, Makromol. Chem., 66, 1963, p 102.
18. H. H. Horowitz and G. Metzger, Analyt. Chem., 35, 1963, p 1464.
19. R. W. Farmer, ASD-TDR-62-1043, Part I, Wright-Patterson Air Force Base, Ohio, 1963.
20. L. Reich, Polymer Letters, 2, 1964, p 621.
21. T. Ozawa, Bull. Chem. Soc., Japan, 38(11), 1965, p 1881.
22. S. L. Madorsky and S. Straus, J. Res. Nat. Bur. Standards, 40, 1948, p 417.

REFERENCES (CONT)

23. I. J. Goldfarb and R. McGuchan, Thermal Degradation of Polyesters, Pt II, Aromatic, AFML-TR-68-182, Part II, Air Force Material Laboratory, Wright-Patterson AFB, Ohio. (To be published)
24. A. E. Newkirk, Anal. Chem., 32, 1960, p 1558.
25. P. D. Garn, Thermoanalytical Methods of Investigation, Academic Press, New York, London, 1965.
26. L. A. Wall, SPE Journal, 9(1), 1960, p 1031.
27. I. J. Goldfarb and A. C. Meeks, AFML-TR-66-375, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, 1967.
28. H. G. McAdie, Anal. Chem., 35, 1963, p 1840.
29. S. L. Madorsky, V. E. Hart, S. Straus, and V. A. Sedlack, J. Res. Nat. Bur. Standards, 51, 1953, p 327.
30. L. A. Wall and J. D. Michaelson, J. Res. Nat. Bur. Standards, 1956, p 27.
31. H. C. Anderson, Makromol. Chem., 51, 1962, p 233.
32. S. H. T. Lee, H. Will, and D. W. Levi, Picatinny Arsenal Technical Report 3321, July 1966, AD 635669.
33. B. Carroll and E. P. Manche, J. Appl. Polymer Science, 9, 1965, p 1895.
34. S. Straus and S. L. Madorsky, J. Res. Nat. Bur. Standards, 66A, 1962, p 401.
35. I. J. Goldfarb and A. C. Meeks, Kinetic Analysis of Thermogravimetry, Pt I, Isothermal, AFML-TR-68-181, Part I, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio.
36. I. J. Goldfarb and R. McGuchan, Thermal Degradation of Polyesters, Pt I, Aliphatic, AFML-TR-68-182, Part I, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio. (To be published)
37. A. Broido, Polymer Letters, 6, 1968, p 349.
38. S. Straus and L. A. Wall, J. Res. Nat. Bur. Standards, 60, 1958, p 39.
39. I. J. Goldfarb and A. C. Meeks, Thermal Degradation of Polyamides, Pt I, Aliphatic, AFML-TR-68- , Pt I, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. (To be published)
40. I. J. Goldfarb and A. C. Meeks, Thermal Degradation of Polyamides, Pt II, Aromatic, AFML-TR-68- , Pt II, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio. (To be published)



## APPENDIX I

### TYPICAL INPUT CARD DECK

## Part II

WEEKS 10TF		19703/68	TEFLON (NEW BAL.)		1.00	.0025	.003	.418	.625					
10TF	WEEKS	0.0	10981	418	1.0	10981	424	2.0	10981	430	3.0	10981	436	
10TF	WEEKS	4.0	10980	441	5.0	10980	447	6.0	10980	453	7.0	10979	458	
10TF	WEEKS	8.0	10977	484	9.0	10975	489	10.0	10972	493	11.0	10969	498	
10TF	WEEKS	12.0	10961	483	13.0	10952	490	14.0	10950	493	15.0	10927	501	
10TF	WEEKS	15.5	10900	505	16.0	10881	507	16.5	10874	510	17.0	10855	512	
10TF	WEEKS	17.5	10802	515	18.0	10768	517	18.5	10722	521	19.0	10670	524	
10TF	WEEKS	19.1	10681	520	19.2	10649	527	19.3	10637	528	19.4	10624	528	
10TF	WEEKS	19.5	10610	529	19.6	10599	529	19.7	10589	530	19.8	10572	530	
10TF	WEEKS	19.9	10558	531	20.0	10540	532	20.1	10528	532	20.2	10510	532	
10TF	WEEKS	20.3	10493	533	20.4	10477	534	20.5	10457	535	20.6	10441	535	
10TF	WEEKS	20.7	10422	536	20.8	10403	537	20.9	10384	537	21.0	10362	537	
10TF	WEEKS	21.1	10344	538	21.2	10325	539	21.3	10301	539	21.4	10279	540	
10TF	WEEKS	21.5	10255	540	21.6	10232	541	21.7	10207	541	21.8	10181	542	
10TF	WEEKS	21.9	10158	542	22.0	10130	543	22.1	10103	544	22.2	10074	544	
10TF	WEEKS	22.3	10044	545	22.4	10017	545	22.5	9984	546	22.6	9944	546	
10TF	WEEKS	22.7	9915	546	22.8	9880	547	22.9	9848	548	23.0	9810	549	
10TF	WEEKS	23.1	9778	549	23.2	9745	549	23.3	9706	550	23.4	9669	550	
10TF	WEEKS	23.5	9627	551	23.6	9591	551	23.7	9550	552	23.8	9507	553	
10TF	WEEKS	23.9	9466	553	24.0	9419	554	24.1	9377	554	24.2	9333	554	
10TF	WEEKS	24.3	9289	555	24.4	9241	556	24.5	9190	556	24.6	9144	557	
10TF	WEEKS	24.7	9093	558	24.8	9042	559	24.9	8989	559	25.0	8917	559	
10TF	WEEKS	25.1	8865	560	25.2	8809	560	25.3	8755	560	25.4	8695	561	
10TF	WEEKS	25.5	8636	562	25.6	8577	562	25.7	8515	563	25.8	8454	563	
10TF	WEEKS	25.9	8382	564	26.0	8327	564	26.1	8265	565	26.2	8198	566	
10TF	WEEKS	26.3	8130	567	26.4	8064	567	26.5	7992	568	26.6	7908	568	
10TF	WEEKS	26.7	7830	569	26.8	7758	569	26.9	7682	570	27.0	7600	570	
10TF	WEEKS	27.1	7530	570	27.2	7451	571	27.3	7370	571	27.4	7275	572	
10TF	WEEKS	27.5	7210	572	27.6	7134	573	27.7	7050	574	27.8	6961	574	
10TF	WEEKS	27.9	6878	573	28.0	6782	573	28.1	6690	570	28.2	6613	577	
10TF	WEEKS	28.3	6523	577	28.4	6438	578	28.5	6342	579	28.6	6259	579	
10TF	WEEKS	28.7	6168	580	28.8	6078	580	28.9	5983	580	29.0	5882	581	
10TF	WEEKS	29.1	5775	582	29.2	5688	582	29.3	5594	582	29.4	5492	584	
10TF	WEEKS	29.5	5381	584	29.6	5290	585	29.7	5193	585	29.8	5089	586	
10TF	WEEKS	29.9	4984	587	30.0	4881	587	30.1	4774	588	30.2	4667	589	
10TF	WEEKS	30.3	4562	590	30.4	4460	590	30.5	4350	590	30.6	4231	590	
10TF	WEEKS	30.7	4147	591	30.8	4046	591	30.9	3930	592	31.0	3823	593	
10TF	WEEKS	31.1	3727	594	31.2	3622	594	31.3	3510	594	31.4	3418	595	
10TF	WEEKS	31.5	3310	596	31.6	3220	596	31.7	3117	597	31.8	3023	597	
10TF	WEEKS	31.9	2912	598	32.0	2795	599	32.1	2707	599	32.2	2617	600	
10TF	WEEKS	32.3	2523	600	32.4	2434	601	32.5	2340	601	32.6	2262	602	
10TF	WEEKS	32.7	2180	603	32.8	2100	603	32.9	2021	604	33.0	1930	604	
10TF	WEEKS	33.1	1867	605	33.2	1791	605	33.3	1723	605	33.4	1658	606	
10TF	WEEKS	33.5	1590	608	33.6	1530	609	33.7	1465	609	33.8	1410	610	
10TF	WEEKS	33.9	1380	610	34.0	1310	610	34.1	1265	610	34.2	1212	611	
10TF	WEEKS	34.3	1182	612	34.4	1143	612	34.5	1120	612	34.6	1072	614	
10TF	WEEKS	34.7	1052	614	34.8	1027	615	34.9	1004	615	35.0	954	616	
10TF	WEEKS	35.1	970	616	35.2	938	617	35.3	940	618	35.4	932	618	
10TF	WEEKS	35.5	926	619	35.6	923	620	35.7	920	620	35.8	920	620	
10TF	WEEKS	35.9	920	620	36.0	920	621	36.1	920	621	36.2	920	623	
10TF	WEEKS	1	36.3	920	624	36.4	920	624	36.5	920	625	36.6	920	625



AFML-TR-68-181  
Part II

## APPENDIX II

### COMPLETE RATE OF WEIGHT LOSS PROGRAM

TGA	PLOT	- EFN	SOURCE STATEMENT	- IFN(S)	-	10/30/68
C			PROGRAM TO DETERMINE RATES OF WEIGHT LOSS AT ONE PERCENT WEIGHT LOSS			
C			INTERVALS FROM THERMOGRAVIMETRIC ANALYSIS DATA.			
C			INPUT TEMPERATURES ARE FITTED TO A FIFTH DEGREE POLYNOMIAL USING A			
C			LEAST SQUARES SUBROUTINE (PLSQ).			
C			WEIGHTS CORRESPONDING TO SHORT TEMPERATURE RANGES ARE FITTED TO A			
C			QUADRATIC BY PLSQ.			
C			INPUT WEIGHTS DIFFERING FROM FITTED LINE BY MORE THAN ONE PERCENT OF THE			
C			TOTAL WEIGHT LOSS ARE REPLACED BY THE CURVE FIT VALUE.			
C			OUTPUT DATA IS PUNCHED ON TO CARDS FOR FURTHER PROCESSING (TO CALCULATE			
C			ACTIVATION ENERGY ETC).			
C			INPUT DATA. SPEED=CHART SPEED IN INCHES PER MINUTE, OFFSET=PEN SEPARATION			
C			IN INCHES. ITI=INITIAL TEMPERATURE READING, ITF=FINAL TEMP. READING.			
C			INDEX LBJ IS SET EQUAL TO 1 TO SIGNAL LAST CARD OF A RUN			
C						
			DIMENSION T(1500),W(1500),TEMP(1500),WW(105),TNW(105),DWD(105),			
			.X(50),Y(50),C(10),A(1),PLOT(50,105),Z(50),TDER(105),TPOLY(105),			
			.RTMP(105)			
		1	READ (5,1000) ID,DATE1,DATE2,COM1,COM2,COM3,COM4, SPEED,OFFSET,			
			.XRANGE,ITI,ITF			1
			CHART = 2.545454*SPEED			
			WRITE (6,3000)			5
			WRITE (6,3050) ID,DATE1,DATE2,COM1,COM2,COM3,COM4			6
			WRITE (6,3060) SPEED			7
			WRITE (6,3065) CHART			8
			WRITE (6,3070) OFFSET			9
			WRITE (6,3080) XRANGE			10
			WRITE (6,3090) ITI			11
			WRITE (6,3100) ITF			12
			N = 0			
C						
C			START LOOP TO READ IN DATA CARDS			
C						
			DO 30 I=1,2995,4			
			N = N+4			
			READ (5,1010) LBJ,T(I),W(I),TEMP(I),T(I+1),W(I+1),TEMP(I+1),			
			.T(I+2),W(I+2),TEMP(I+2),T(I+3),W(I+3),TEMP(I+3)			
C						
C			T = TIME (IN INCHES), W = WEIGHT, TEMP = TEMPERATURE			
C						17
			IF (LBJ.EQ.1) GO TO 40			
		30	CONTINUE			
		40	NL = N-4			
C						
C			START LOOP TO CALCULATE NUMBER OF DATA READ IN			
C						
			DO 50 I=NL,N			
			IF (T(I).NE.0.0) GO TO 50			
			N = I-1			
			GO TO 51			
		50	CONTINUE			
		51	JJ = .030*FLOAT(N)			
			LL = MAX0(JJ,10)			
C						
C			JJ = 3 PERCENT OF NO. OF DATA SETS READ IN			

	TGA	PLOT - EFN SOURCE STATEMENT - IFN(S) -	10/30/68
C	LL = NO. OF CURVE FIT POINTS (LATER = NN)		
C	WRITE (6,3170) LL		52
	WRITE (6,3010) N		53
	NN = LL		
C	K = POLYNOMIAL ORDER, NEEDED FOR PLSQ SUBROUTINE. LIST = 0 FOR NO ERROR		
C	ANALYSIS OF PLSQ		
C	D = TOTAL WEIGHT LOSS		
C	K = 2		
	LIST = 0		
	LINDA = 1		
	D = W(1) - W(N)		
	DO 55 I=1,N		
	W(I) = 100.-(100.*(W(I)-W(N))/D)		
C	CONVERT TIME IN INCHES TO MINUTES		
C	T(I) = T(I)/SPEED		
	55 CONTINUE		
C	DT = PEN SEPARATION IN MINUTES.		
C	DT = SPEED*OFFSET		
C	START MAJOR LOOP		
C	DO 100 NW = 1,99		
	58 II = LINDA-1		
	WW(NW) = FLOAT(NW)		
C	SCAN WEIGHT DATA FOR ONE CLOSE TO BUT JUST GREATER THAN ONE PERCENT WEIGHT		
C	LOSS. II = INDEX OF THAT POINT		
C	DO 60 I=LINDA,N		
	II = II+1		
	IF (W(I).GT.WW(NW)) GO TO 70		
	60 CONTINUE		
	70 LINDA = II-(LL/2)		
C	LINDA = INDEX OF FIRST DATA TO BE USED BY PLSQ		
C	DO 80 J=1,LL		
	J1 = LINDA+J-1		
	X(J) = T(J1)		
	Y(J) = W(J1)		
	Z(J) = TEMP(J1)		
	80 CONTINUE		
C	CURVE FIT OF TIME AND WEIGHT DATA		
C	CALL PLSQ (X,Y,NN,K,C,LIST,EMAX,ERMS,EMEQ)		100
	KK = 1		
C	START LOOP TO CHECK FOR BAD INPUT DATA		

TGA	PLOT	- EFN	SOURCE STATEMENT	- IFN(S)	- 10/30/68
C			DO 81 J=1,LL		
			JI = LINDA+J-1		
C			WE = WEIGHT CALCULATED FROM POLYNOMIAL		
C			WE = C(1)*T(JI)**2+C(2)*T(JI)+C(3)		
C			COMPARE CALCULATED AND ORIGINAL DATA		
C			IF (ABS(WE-W(JI)).GT.1.) GO TO 82		
			GO TO 81		
			82 WRITE (6,4000) JI,W(JI),WE		
C			REPLACE BAD DATA BY CALCULATED VALUES		
C			W(JI) = WE		114
			KK = 2		
			81 CONTINUE		
			GO TO (83,58),KK		
C			CHECK FOR IMAGINARY ROOTS IN SOLUTION OF QUADRATIC		
C			83 SCREW = C(2)*C(2)-4.0*C(1)*(C(3)-WW(NW))		
			IF (SCREW.LT.0.0) GO TO 90		
C			USE REAL ROOT TO DETERMINE TIME CORRESPONDING TO EACH PERCENT WEIGHT LOSS		
C			TNW(NW) = (SQRT(C(2)*C(2)-4.0*C(1)*(C(3)-WW(NW)))-C(2))/(2.0*C(1))		
C			DWDT = RATE OF WEIGHT LOSS		
C			DWDT(NW) = 2.0*C(1)*TNW(NW) + C(2)		126
			GO TO 100		
			90 TNW(NW) = T(II-1)		
			DWDT(NW) = 0.0		
			TA = T(II)*SPEED		
C			WRITE OUT IDENTIFICATION AND LOCATION OF BAD DATA		
C			WRITE (6,3160) NW,II,TA,W(II)		136
			100 CONTINUE		
			K = 5		
C			CURVE FIT OF TIME AND TEMPERATURE DATA		
C			CALL PLSQ(T,TEMP,N,K,C,LIST,EMAX,ERMS,EMEQ)		142
			WRITE (6,5100) EMAX		143
			WRITE (6,5200) ERMS		144
			WRITE (6,5300)		145
			WRITE (6,5400) (C(I),I=1,6)		146
			WRITE (6,3110)		153
			DO 120 NW=1,99		
C			CT = CORRECTED TIME, USED TO FIND TIME AT EACH TEMPERATURE		

TGA		10/30/68	
PLOT - EFN SOURCE STATEMENT - IFN(S) -			
	CT = TNW(NW)-DT		
	TSTOR = C(1)		
C			
C	LOOP TO EVALUATE TEMPERATURE POLYNOMIAL FOR EACH VALUE OF CT		
C			
	DO 200 I=2,6		
200	TSTOR = TSTOR*CT+C(I)		
	TPOLY(NW) = TSTOR		
	TSTOR = 5.*C(1)		
	DO 250 I=2,5		
	J = 6-I		
250	TSTOR = TSTOR*CT+FLOAT(J)*C(I)		
C			
C	TDER = TEMPERATURE DERIVATIVE		
C	RTEMP = RECIPROCAL OF ABSOLUTE TEMPERATURE		
C			
	TDER(NW) = TSTOR		
	RTEMP(NW) = 1.0/(TPOLY(NW)+273.16)		
	WRITE (6,3120) NW,DWDI(NW),TPOLY(NW),TDER(NW),RTEMP(NW)		172
120	CONTINUE		
	STDER = 0.0		
C			
C	CALCULATE AVERAGE TEMPERATURE DERIVATIVE (AVE)		
C			
	DO 125 I=1,99		
	STDER = STDER + TDER(I)		
125	CONTINUE		
	AVE = STDER/99.0		
	WRITE (6,3125) AVE		
C			
C	SET UP DUMMY POINTS FOR GRAPH PLOTTING SUBROUTINE (GP)		
C			187
	WW(100) = 0.0		
	DWDI(100) = 0.0		
	TNW(100) = TNW(99)		
	TDER(100) = 0.0		
	WW(101) = 100.0		
	DWDI(101) = 0.0		
	TNW(101) = TNW(99)		
	TDER(101) = TDER(99)		
	WRITE (6,3000)		188
	WRITE (6,3130) ID		189
	L = 3		
	LS = 5		
	LW = 101		
	LN = 50		
	M = 101		
	DATA A/1H./		
	JN = 1		
C			
C	PLOT GRAPH OF RATE OF WEIGHT LOSS AGAINST PERCENT WEIGHT LOSS		
C			
	CALL GP (WW,DWDI,L,LS,M,JN,LW,LN,A,PLOT)		196
	WRITE (6,3000)		197
	WRITE (6,3140) ID		
C			

TGA	10/30/68
PLOT - EFN SOURCE STATEMENT - IFN(S) -	
C PLOT GRAPH OF PERCENT WEIGHT LOSS AGAINST TIME	
C CALL GP (TNW,WW,L,LS,M,JN,LW,LN,A,PLOT)	198
WRITE (6,3000)	199
WRITE (6,3150) ID	200
C PLOT GRAPH OF TEMPERATURE DERIVATIVE AGAINST TIME	
C CALL GP (TNW,TDER,L,LS,M,JN,LW,LN,A,PLOT)	201
DWDT(100) = 0.0	202
TPOLY(100) = 0.0	
C PUNCH OUTPUT CARDS CONTAINING PERCENT WT. LOSS(NW) THEN THREE PAIRS OF	
C TEMPERATURE AND RATE OF WEIGHT LOSS DATA	
C DO 150 NW=1,100,3	
PUNCH 5000,ID,NW,DWDT(NW),TPOLY(NW),DWDT(NW+1),TPOLY(NW+1),	
.DWDT(NW+2),TPOLY(NW+2)	206
150 CONTINUE	
C LOOK FOR FURTHER SETS OF DATA IF NEXT CARD CONTAINS A ONE IN COLUMN 10	
C READ (5,1020) MORE	215
IF (MORE.EC.1) GO TO 1	
STOP	
1000 FORMAT(8X,A4,2X,A6,A2,2X,A6,A6,A6,A3,F7.4,2X,F5.4,2X,F6.2,3X,	
.I3,3X,I3)	
1010 FORMAT(13X,I1,2X,3(F6.2,F5.1,1X,F4.0),F6.2,F5.1,1X,F4.0)	
1020 FORMAT (9X,I1)	
1030 FORMAT (I2)	
3000 FORMAT (1H1)	
3010 FORMAT (10X,21HTOTAL NO OF POINTS = ,I4)	
3050 FORMAT(5X,A4,8X,A6,A2,10X,A6,A6,A6,A3//)	
3060 FORMAT (10X,33HCHART SPEED (INCHES PER MINUTE) =,F6.4)	
3065 FORMAT (10X,38HCHART SPEED (FURLONGS PER FORTNIGHT) =,F7.4)	
3070 FORMAT (10X,17HOFFSET (INCHES) =,F7.4)	
3080 FORMAT (10X,17HXRANGE (INCHES) =,F7.2)	
3090 FORMAT (10X,18HINITIAL TEMP (C) =,I5)	
3100 FORMAT (10X,16HFINAL TEMP (C) =,I5)	
3106 FORMAT (18X,I5,4X,F9.3,4X,F7.2,4X,F8.2)	
3110 FORMAT (/3X,11HWEIGHT LOSS,6X,8HDWDT(NW),13X,5HTPOLY,6X,	
.4HTDER,11X,5HRTMP)	
3120 FORMAT (6X,I3,10X,E12.5,7X,F9.3,2E15.5)	
3125 FORMAT (/10X,27H AVERAGE TEMP DERIVATIVE = ,E15.5)	
3130 FORMAT (10X,19HDWDT VS WEIGHT LOSS,20X,A4)	
3140 FORMAT (10X,19HWEIGHT LOSS VS TIME,20X,A4)	
3150 FORMAT (10X,12HTDER VS TIME,20X,A4)	
3160 FORMAT(2X,17HSCREW LESS THAN 0,10X,3HNW=,I3,10X,3HII=,I4,10X,	
.2HT=,F6.2,10X,2HW=,F5.1)	
3170 FORMAT (10X,25HNO OF PTS IN CURVE FIT = ,I2)	
4000 FORMAT (10X,9HAT PT NO ,I4,10H WEIGHT = ,F5.1,13H REPLACED BY ,	
.F5.1)	
5000 FORMAT (2X,A4,I4,E13.5,F6.1,E13.5,F6.1,E13.5,F6.1)	
5100 FORMAT (10X,17HMAX TEMP ERROR = ,F10.6)	
5200 FORMAT (10X,30HTEMP ROOT MEAN SQUARE ERROR = ,F10.6)	
5300 FORMAT (10X,15HTEMP POLY COEFF)	
TGA	
PLOT - EFN SOURCE STATEMENT - IFN(S) -	
5400 FORMAT(13X,F10.6)	
END	

AFML-TR-68-181  
Part II

### APPENDIX III

#### PUNCHED CARD OUTPUT FROM RATE PROGRAM

AFML-TR-68-181  
Part II

10TF		338		TEFLON DEGRADATION					
10T	1	0.43704E-00	507.9	0.78487E	00	518.1	0.10301E	01	524.9
10T	4	0.13932E	01 529.2	0.17180E	01	532.9	0.19348E	01	538.0
10T	7	0.22448E	01 538.7	0.25593E	01	541.1	0.29221E	01	549.2
10T	10	0.32235E	01 548.0	0.34049E	01	548.7	0.35238E	01	548.9
10T	13	0.37758E	01 549.7	0.40296E	01	551.3	0.42182E	01	552.7
10T	16	0.44440E	01 554.0	0.48274E	01	559.2	0.50011E	01	556.4
10T	19	0.53156E	01 557.5	0.55208E	01	558.5	0.56799E	01	559.5
10T	22	0.57782E	01 560.5	0.58077E	01	561.1	0.59939E	01	562.4
10T	25	0.61520E	01 563.3	0.63136E	01	564.2	0.65319E	01	565.1
10T	28	0.68436E	01 566.0	0.70771E	01	566.7	0.72450E	01	567.9
10T	31	0.74898E	01 568.3	0.75789E	01	569.0	0.76239E	01	569.7
10T	34	0.76522E	01 570.4	0.77316E	01	571.2	0.78633E	01	571.5
10T	37	0.83340E	01 572.6	0.82487E	01	573.3	0.83946E	01	574.0
10T	40	0.85006E	01 574.8	0.85109E	01	575.2	0.87108E	01	575.9
10T	43	0.87438E	01 578.5	0.87808E	01	577.2	0.88180E	01	577.8
10T	46	0.88743E	01 578.4	0.91130E	01	577.0	0.92282E	01	579.8
10T	49	0.94210E	01 580.2	0.95133E	01	580.0	0.97193E	01	581.4
10T	52	0.97623E	01 581.9	0.97623E	01	582.5	0.97440E	01	583.1
10T	55	0.97178E	01 583.7	0.99691E	01	584.2	0.10033E	02	584.8
10T	58	0.10131E	02 585.4	0.10208E	02	585.9	0.10281E	02	586.4
10T	61	0.10408E	02 587.0	0.10414E	02	587.5	0.10578E	02	588.0
10T	64	0.10310E	02 588.8	0.10204E	02	589.1	0.10352E	02	589.7
10T	67	0.10344E	02 590.2	0.10338E	02	590.3	0.10391E	02	591.3
10T	70	0.10387E	02 591.5	0.10423E	02	592.4	0.10488E	02	592.9
10T	73	0.10321E	02 593.4	0.10237E	02	594.0	0.10399E	02	594.3
10T	76	0.10011E	02 593.1	0.10151E	02	595.7	0.10124E	02	595.2
10T	79	0.10033E	02 596.8	0.99414E	01	597.3	0.97907E	01	597.5
10T	82	0.98724E	01 598.3	0.97401E	01	599.0	0.96790E	01	599.8
10T	85	0.88743E	01 600.5	0.84708E	01	601.0	0.82320E	01	601.7
10T	88	0.79913E	01 602.4	0.77573E	01	603.1	0.75090E	01	603.6
10T	91	0.72132E	01 604.6	0.69701E	01	605.4	0.66873E	01	606.3
10T	94	0.59624E	01 607.2	0.54449E	01	608.2	0.48992E	01	609.4
2 10T	97	0.41379E	01 610.7	0.33280E	01	612.5	0.29121E	01	614.4



APPENDIX IV

COMPLETE PROGRAM FOR THE DETERMINATION OF  
ARRHENIUS PARAMETERS BY FRIEDMAN'S METHOD

TGA		06/13/68	
PLOT - EFN SOURCE STATEMENT - IFN(S) -			
C	PROGRAMME TO DETERMINE TGA PARAMETERS BY FRIEDMANS METHOD		
C	PROGRAMME ACCEPTS DATA CARDS HAVING THREE SETS OF DATA PER CARD.		
C	LAST CARD OF EACH DECK MUST HAVE A ONE IN COLUMN 1. LAST CARD OF		
C	LAST DECK FOR ONE POLYMER SYSTEM MUST HAVE A TWO IN COLUMN 1 INSTEAD		
C	TO RUN A SECOND SET OF DECKS, PUNCH A CARD WITH A THREE IN COLUMN 1		
C	AND PLACE BETWEEN SETS		
C	AT THE END OF ALL DECKS PLACE A BLANK CARD THEN AN \$EOF		
C			
C	SYMBOLS DWDT = RATE OF WEIGHT LOSS, RTEMP = RECIPROCAL OF ABSOLUTE		
C	TEMPERATURE, RATE = LOG RATE OF WEIGHT LOSS, SLOPE = SLOPE OF ARRHENIUS		
C	PLOT, PREFX = PRE-EXPONENTIAL FACTOR, PLOT = DIMENSION OF GP SUBROUTINE		
C	ACTE = ACTIVATION ENERGY, X AND Y REPRESENT DATA TREATED BY GP		
C	TPOLY = INPUT TEMPERATURES, ID = IDENTIFICATION, A = NO. OF SYMBOLS IN GP		
C	AA = PERCENT WEIGHT LOSS, AFW = FUNCTION FROM FRIEDMANS EQUATION		
C	FW = AVERAGE AFW, RB = LOG (PERCENT RESIDUE), WF = AVERAGE AFW		
C			
	DIMENSION DWDT(100,10),RTEMP(100,10),RATE(100,10),SLOPE(100),		
	.PREX(100),PLOT(50,100),ACTE(100),X(10),Y(10),		
	.TPOLY(100,10),ID(10),A(1),AA(100),AFW(10),FW(100),RB(95),WF(95),		
	.SPS(100),SDS(100),SDI(100)		
1	READ (5,1000) IG,COM1,COM2,COM3,COM4,COM5,COM6,COM7,COM8	1	
	WRITE (6,3000)	3	
	WRITE (6,1100) IG,COM1,COM2,COM3,COM4,COM5,COM6,COM7,COM8	4	
2	J = 0		
10	J = J+1		
C			
C	START LOOP TO READ IN DATA		
C			
	DO 20 NW = 1, 97, 3		
C			
C	LRJ = 1 IN COLUMN 1 OF LAST CARD OF A DECK, LAST CARD OF LAST DECK FOR		
C	ONE POLYMER SYSTEM NEEDS LRJ = 2.		
C			
	READ (5,1200) LRJ,ID(J),IW,DWDT(NW,J),TPOLY(NW,J),DWDT(NW+1,J),		
	.TPOLY(NW+1,J),DWDT(NW+2,J),TPOLY(NW+2,J)		
C			
C	CHECK THAT INPUT CARDS ARE IN CONSECUTIVE ORDER		
C		10	
	IF (IW-NW) 3,4,3		
3	WRITE (6,1900) NW,ID(J),IW		
	STOP	21	
4	AA(NW) = FLOAT(NW)		
	AA(NW+1) = FLOAT(NW+1)		
	AA(NW+2) = FLOAT(NW+2)		
	IF (LRJ.EQ.1) GO TO 10		
20	IF (LRJ.EQ.2) GO TO 25		
25	XJ = J		
C			
C	WRITE LIST OF RUN IDS		
C			
	WRITE (6,1800)(ID(I),I=1,J)		
C			
C	CHECK FOR AT LEAST THREE DATA DECKS		
C		36	
	IF (J-3) 30,35,35		

06/13/68

TGA	PLOT	EFN	SOURCE STATEMENT	IFN(S)
			30 WRITE (6,2000)	44
			GO TO 300	
			35 WRITE (6,1500)	45
			TSUM = 0	
			N = 0	
			SPREX = 0.0	
C				
C			START LOOP TO CALCULATE LEAST SQUARES LINE OF LOG(RATE) VS. RTEMP	
C				
			DO 45 NW = 4,98	
			SUMXX = 0	
			SUMYY = 0	
			SUMX = 0	
			SUMY = 0	
			SUMXY = 0	
			DO 40 K = 1,J	
C				
C			CHECK FOR ZERO RATES	
C				
			IF(DWDI(NW,K).LT.1.0E-10) GO TO 65	
			RATE(NW,K) = ALOG10(DWDI(NW,K))	53
			RTEMP(NW,K) = 1.0/(TPOLY(NW,K)+273.16)	
C				
C			SUMXX = PARTIAL SUM OF X SQUARED ETC.	
C				
			SUMXX = SUMXX + RTEMP(NW,K)**2	
			SUMYY = SUMYY + (RATE(NW,K))**2	
			SUMX = SUMX + RTEMP(NW,K)	
			SUMY = SUMY + RATE(NW,K)	
			40 SUMXY = SUMXY + RTEMP(NW,K)*RATE(NW,K)	
			GO TO 55	
C				
C			SET UP DUMMY POINTS FOR GP IF A DWDI VALUE IS ZERO	
C				
			65 ACTE(NW) = 0.	
			PREX(NW) = 0.	
			RATE (NW,K) = 0.	
			RTEMP (NW,K) = 0.0015	
			GO TO 45	
			55 SLOPE(NW) = (XJ*SUMXY-SUMX*SUMY)/(XJ*SUMXX-SUMX**2)	
			SPS(NW) = ((SUMYY-(SUMY*SUMY/XJ))-((XJ*SUMXY-SUMX*SUMY)**2/	
			.(XJ*XJ*SUMXX-XJ*SUMX*SUMX)))/(XJ-2.0))	
			ALPHA = (SPS(NW)/(SUMXX-(SUMX*SUMX/XJ)))*4.576	
			IF(ALPHA) 58,58,57	
			57 SDS(NW) = SQRT(ALPHA)	85
			GO TO 59	
			58 SDS(NW) = 0.0	
			59 RETA = (SPS(NW)*SUMXX/(XJ*SUMXX-SUMX*SUMX))	
			IF(RETA) 62,62,61	
			61 SDI(NW) = SQRT(RETA)	94
			GO TO 63	
			62 SDI(NW) = 0.0	
			63 ACTE(NW) = -SLOPE(NW)*4.576	
			PREX(NW) = (SUMXX*SUMY-SUMX*SUMXY)/(XJ*SUMXX-SUMX**2)	
			IF(NW.LT.10) GO TO 45	
			IF(NW.GT.80) GO TO 45	

TGA

PLOT

-

EFN

SOURCE STATEMENT

-

IFN(S)

-

06/13/68

TSUM = TSUM-SLOPE(NW)

SPREX = SPREX + PREX(NW)

N = N+1

45 CONTINUE

C

C

C

CALCULATE AVERAGE ACTIVATION ENERGY AND PRE-EXPONENTIAL FACTOR

AVPREX = SPREX / FLOAT(N)

AVEA = TSUM/FLOAT(N)

AVACTE = AVEA\*1.987\*2.303

C

C

C

START LOOP TO CALCULATE AFW

DO 70 NW = 4,98

Z = 0

DO 90 K = 1,J

AFW(K) = RATE(NW,K) + AVEA\*RTMP(NW,K)

90 Z = Z + AFW(K)

FW(NW) = Z/XJ

WN = FLOAT(NW)

GG = ALOG10(100.-WN)

SD = 0

126

DO 93 K = 1,J

93 SD = SD + (FW(NW)-AFW(K))\*\*2

YK = J-1

SDAFW = SQRT(SD/YK)

C

C

C

C

WRITE OUT RESULTS PERCENT WT. LOSS, ACTIVATION ENERGY, PRE-EXPONENTIAL  
FACTOR, AVERAGE FW, AND STANDARD DEVIATIONS, ALSO LOG WEIGHT REMAINING(GG)

70 WRITE (6,1400) NW,ACTE(NW),SDS(NW),PREX(NW),SDI(NW),FW(NW),SDAFW,

133

.GG

WRITE (6,1425) AVACTE

134

WRITE (6,1435) AVPREX

141

WRITE (6,1440)

142

C

C

C

SET UP INFORMATION FOR GP SUBROUTINE, SEE OTHER PROGRAMS

L = 3

143

LS = 5

LW = 100

LN = 50

M = J

DATA A/IH./

JN = 1

C

C

C

START LOOP FOR PLOTTING GRAPHS AT 10 PERCENT WEIGHT LOSS INTERVALS

DO 200 NW = 10,99,10

DO 100 K = 1,J

X(K) = RTEMP(NW,K)

100 Y(K) = RATE(NW,K)

WRITE (6,3000)

150

WRITE (6,1700) NW

C

C

PLOT GRAPH OF LOG (RATE OF WEIGHT LOSS) AGAINST RECIPROCAL

TGA		06/13/68	
PLOT	- EFN	SOURCE STATEMENT	- IFN(S) -
C		OF TEMPERATURE	
C			161
		200 CALL GP (X,Y,L,LS,M,JN,LW,LN,A,PLOT)	162
		M = 100	
		WRITE (6,3000)	167
		WRITE (6,3100)	
C			
C		PLOT GRAPH OF ACTIVATION ENERGY AGAINST PERCENT WT. LOSS	
C			168
		CALL GP (AA,ACTE,L,LS,M,JN,LW,LN,A,PLOT)	169
		WRITE (6,3000)	170
		WRITE (6,3200)	
C			
C		PLOT GRAPH OF PRE-EXPONENTIAL FACTOR AGAINST PERCENT WEIGHT LOSS	
C			171
		CALL GP (AA,PREX,L,LS,M,JN,LW,LN,A,PLOT)	172
		WRITE (6,3000)	173
		WRITE (6,3300)	174
		DO 75 I=1,87	
		BB(I) = ALOG10(100.-AA(I+3))	175
		75 WF(I) = FW(I+3)	
		LW = 95	
		M = 87	
C			
C		PLOT GRAPH OF LOG(AFW) AGAINST LOG(PERCENT RESIDUE WEIGHT)	
C			
		CALL GP(BB,WF,L,LS,M,JN,LW,LN,A,PLOT)	188
		WRITE (6,3000)	
C			
C		LOOK FOR FURTHER SETS OF DATA	
C			189
		300 READ (5,1300) MORE	190
		IF(MORE.EQ.3) GO TO 1	
		90 STOP	
		1000 FORMAT (2X,A3,2X,8A6)	
		1100 FORMAT (10X,A3,2X,8A6)	
		1200 FORMAT (11,1X,A4,I4,E13.5,F6.1,F13.5,F6.1,F13.5,F6.1)	
		1300 FORMAT (11)	
		1400 FORMAT (10X,I3,4X,-3PF7.3,5X,F6.3,5X,OPF6.3,2(5X,F6.3),2(5X,F6.4))	
		1425 FORMAT (/10X,29H AVERAGE ACTIVATION ENERGY = ,-3PF6.3)	
		1435 FORMAT (10X,17H AVERAGE LOG PREX,10X,2H= ,F6.3)	
		1440 FORMAT(10X,34HBOTH FOR 10-90 PERCENT WEIGHT LOSS)	
		1500 FORMAT (/8X,7HWT LOSS,2X,8HEA(KCAL),3X,8HST.DEVN.,3X,8HLOG PREX,	
		.3X,8HST.DEVN.,2X,10HAV.LOG AFW,2X,8HST.DEVN.,2X,11HLOG RES.WT.)	
		1700 FORMAT (10X,18HLOG RATE VS 1/TEMP/10X,14HWEIGHT LOSS = ,I4)	
		1800 FORMAT (/10X,11HRUN ID NOS ,9(A4,2H, ))	
		1900 FORMAT (10X,13HEPERROR FOR W =,I4,7HRUN NO ,A3,6H READ ,I3,	
		.9H INSTEAD.)	
		2200 FORMAT (10X,25HLESS THAN 3 HEATING RATES/1H1)	
		3000 FORMAT (1H1)	
		3100 FORMAT (10X,32HACTIVATION ENERGY VS WEIGHT LOSS)	
		3200 FORMAT (10X,22HPRE-EXP VS WEIGHT LOSS)	
		3300 FORMAT(10X,46HAVER LOG AF(W) VS LOG PERCENT WEIGHT REMAINING)	
		END	

APPENDIX V

RATES OF WEIGHT LOSS FOR A  
TYPICAL TEFLON EXPERIMENT

## Part II

ICTF

19/03/68

TEFLON (NEW BAL.)

CHART SPEED (INCHES PER MINUTE) = 1.0000  
 CHART SPEED (FURLONGS PER FORTNIGHT) = 2.5455  
 OFFSET (INCHES) = 0.0625  
 X RANGE (INCHES) = 36.60  
 INITIAL TEMP (C) = 418  
 FINAL TEMP (C) = 625  
 NO OF PTS IN CURVE FIT = 10  
 TOTAL NO OF POINTS = 200  
 MAX TEMP ERROR = 2.616966  
 TEMP ROOT MEAN SQUARE ERROR = 0.635928  
 TEMP POLY COEFF  
     0.000003  
    -0.000230  
     0.007066  
    -0.087217  
     5.973110  
    418.330875

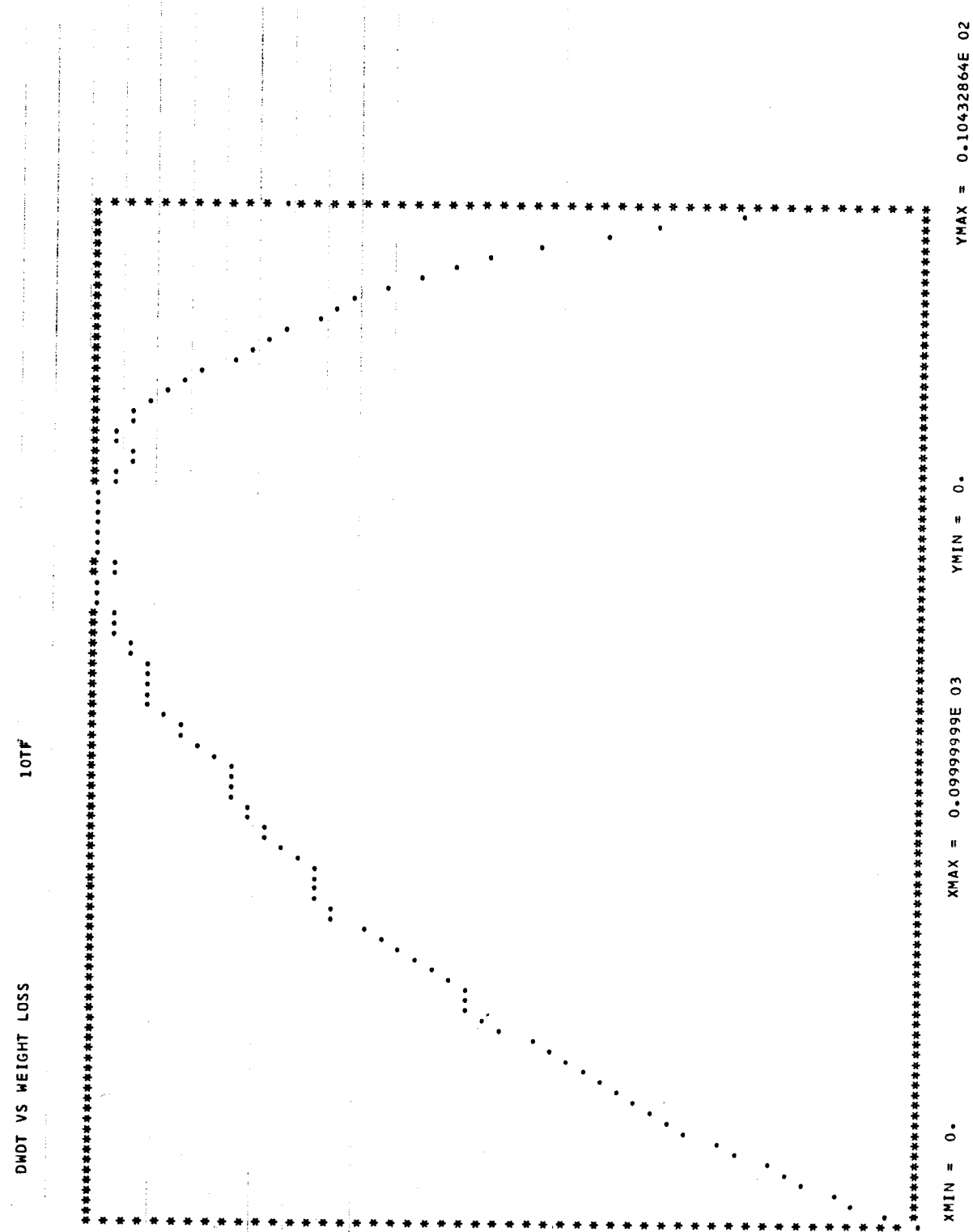
WEIGHT LOSS	CWDT(NW)	TPOLY	TDER	RTEMP
1	0.43704E-00	507.899	0.57000E 01	0.12803E-02
2	0.76467E 00	518.102	0.57125E 01	0.12638E-02
3	0.10531E 01	524.516	0.57103E 01	0.12536E-02
4	0.13932E 01	529.237	0.57040E 01	0.12463E-02
5	0.17160E 01	532.890	0.56964E 01	0.12406E-02
6	0.19640E 01	535.986	0.56884E 01	0.12359E-02
7	0.22448E 01	538.693	0.56803E 01	0.12318E-02
8	0.25599E 01	541.067	0.56724E 01	0.12282E-02
9	0.29225E 01	543.174	0.56649E 01	0.12250E-02
10	0.32235E 01	544.993	0.56581E 01	0.12223E-02
11	0.34049E 01	546.670	0.56516E 01	0.12198E-02
12	0.35286E 01	548.339	0.56449E 01	0.12173E-02
13	0.37758E 01	549.891	0.56385E 01	0.12150E-02
14	0.40299E 01	551.333	0.56326E 01	0.12129E-02
15	0.42162E 01	552.693	0.56269E 01	0.12109E-02
16	0.44440E 01	553.998	0.56214E 01	0.12090E-02
17	0.46574E 01	555.237	0.56162E 01	0.12072E-02
18	0.50011E 01	556.430	0.56113E 01	0.12054E-02
19	0.53156E 01	557.516	0.56068E 01	0.12038E-02
20	0.55268E 01	558.527	0.56027E 01	0.12024E-02
21	0.56799E 01	559.508	0.55988E 01	0.12010E-02
22	0.57782E 01	560.473	0.55950E 01	0.11996E-02
23	0.58077E 01	561.465	0.55912E 01	0.11981E-02
24	0.59939E 01	562.406	0.55877E 01	0.11968E-02
25	0.61520E 01	563.326	0.55843E 01	0.11955E-02
26	0.63133E 01	564.223	0.55812E 01	0.11942E-02
27	0.65319E 01	565.113	0.55782E 01	0.11929E-02
28	0.68436E 01	565.958	0.55754E 01	0.11917E-02
29	0.70771E 01	566.750	0.55729E 01	0.11906E-02
30	0.73456E 01	567.515	0.55707E 01	0.11895E-02
31	0.74898E 01	568.251	0.55686E 01	0.11885E-02
32	0.75789E 01	568.978	0.55666E 01	0.11875E-02
33	0.76239E 01	569.701	0.55648E 01	0.11864E-02
34	0.76522E 01	570.446	0.55631E 01	0.11854E-02
35	0.77316E 01	571.172	0.55615E 01	0.11844E-02
36	0.78633E 01	571.894	0.55601E 01	0.11834E-02
37	0.80040E 01	572.598	0.55588E 01	0.11824E-02
38	0.82437E 01	573.284	0.55577E 01	0.11814E-02
39	0.83949E 01	573.950	0.55568E 01	0.11805E-02

AFML-TR-68-181  
Part II

40	0.85006E 01	574.597	0.55560E 01	0.11796E-02
41	0.85905E 01	575.245	0.55554E 01	0.11787E-02
42	0.87186E 01	575.883	0.55549E 01	0.11778E-02
43	0.87468E 01	576.515	0.55545E 01	0.11769E-02
44	0.87688E 01	577.151	0.55543E 01	0.11760E-02
45	0.88183E 01	577.783	0.55543E 01	0.11752E-02
46	0.88743E 01	578.419	0.55543E 01	0.11743E-02
47	0.91338E 01	579.047	0.55546E 01	0.11734E-02
48	0.92862E 01	579.648	0.55550E 01	0.11726E-02
49	0.94210E 01	580.236	0.55555E 01	0.11718E-02
50	0.95533E 01	580.817	0.55562E 01	0.11710E-02
51	0.97158E 01	581.385	0.55570E 01	0.11702E-02
52	0.97623E 01	581.946	0.55579E 01	0.11694E-02
53	0.97623E 01	582.510	0.55590E 01	0.11687E-02
54	0.97445E 01	583.086	0.55602E 01	0.11679E-02
55	0.97178E 01	583.674	0.55617E 01	0.11671E-02
56	0.99691E 01	584.248	0.55632E 01	0.11663E-02
57	0.10038E 02	584.802	0.55649E 01	0.11656E-02
58	0.10131E 02	585.351	0.55668E 01	0.11648E-02
59	0.10208E 02	585.896	0.55687E 01	0.11641E-02
60	0.10281E 02	586.432	0.55708E 01	0.11633E-02
61	0.10400E 02	586.964	0.55731E 01	0.11626E-02
62	0.10414E 02	587.493	0.55755E 01	0.11619E-02
63	0.10376E 02	588.031	0.55780E 01	0.11612E-02
64	0.10310E 02	588.572	0.55808E 01	0.11605E-02
65	0.10204E 02	589.117	0.55838E 01	0.11597E-02
66	0.10352E 02	589.667	0.55870E 01	0.11590E-02
67	0.10344E 02	590.210	0.55903E 01	0.11583E-02
68	0.10358E 02	590.751	0.55938E 01	0.11575E-02
69	0.10391E 02	591.290	0.55975E 01	0.11568E-02
70	0.10387E 02	591.825	0.56013E 01	0.11561E-02
71	0.10423E 02	592.364	0.56054E 01	0.11554E-02
72	0.10433E 02	592.894	0.56096E 01	0.11547E-02
73	0.10321E 02	593.423	0.56140E 01	0.11540E-02
74	0.10237E 02	593.962	0.56186E 01	0.11532E-02
75	0.10099E 02	594.509	0.56235E 01	0.11525E-02
76	0.10011E 02	595.089	0.56290E 01	0.11517E-02
77	0.10151E 02	595.659	0.56346E 01	0.11510E-02
78	0.10124E 02	596.219	0.56403E 01	0.11502E-02
79	0.10033E 02	596.774	0.56463E 01	0.11495E-02
80	0.99414E 01	597.328	0.56524E 01	0.11488E-02
81	0.97937E 01	597.889	0.56589E 01	0.11480E-02
82	0.96724E 01	598.456	0.56657E 01	0.11473E-02
83	0.94010E 01	599.041	0.56729E 01	0.11465E-02
84	0.90958E 01	599.649	0.56808E 01	0.11457E-02
85	0.86745E 01	600.311	0.56897E 01	0.11449E-02
86	0.84766E 01	600.964	0.56988E 01	0.11440E-02
87	0.82320E 01	601.653	0.57088E 01	0.11431E-02
88	0.79915E 01	602.368	0.57196E 01	0.11422E-02
89	0.77573E 01	603.100	0.57311E 01	0.11412E-02
90	0.75096E 01	603.846	0.57433E 01	0.11402E-02
91	0.72152E 01	604.618	0.57565E 01	0.11392E-02
92	0.68785E 01	605.430	0.57709E 01	0.11382E-02
93	0.64873E 01	606.282	0.57866E 01	0.11371E-02
94	0.59624E 01	607.219	0.58047E 01	0.11359E-02
95	0.54449E 01	608.232	0.58252E 01	0.11346E-02
96	0.48352E 01	609.365	0.58493E 01	0.11331E-02
97	0.41379E 01	610.678	0.58787E 01	0.11314E-02
98	0.33280E 01	612.262	0.59164E 01	0.11294E-02
99	0.23131E 01	614.390	0.59709E 01	0.11267E-02

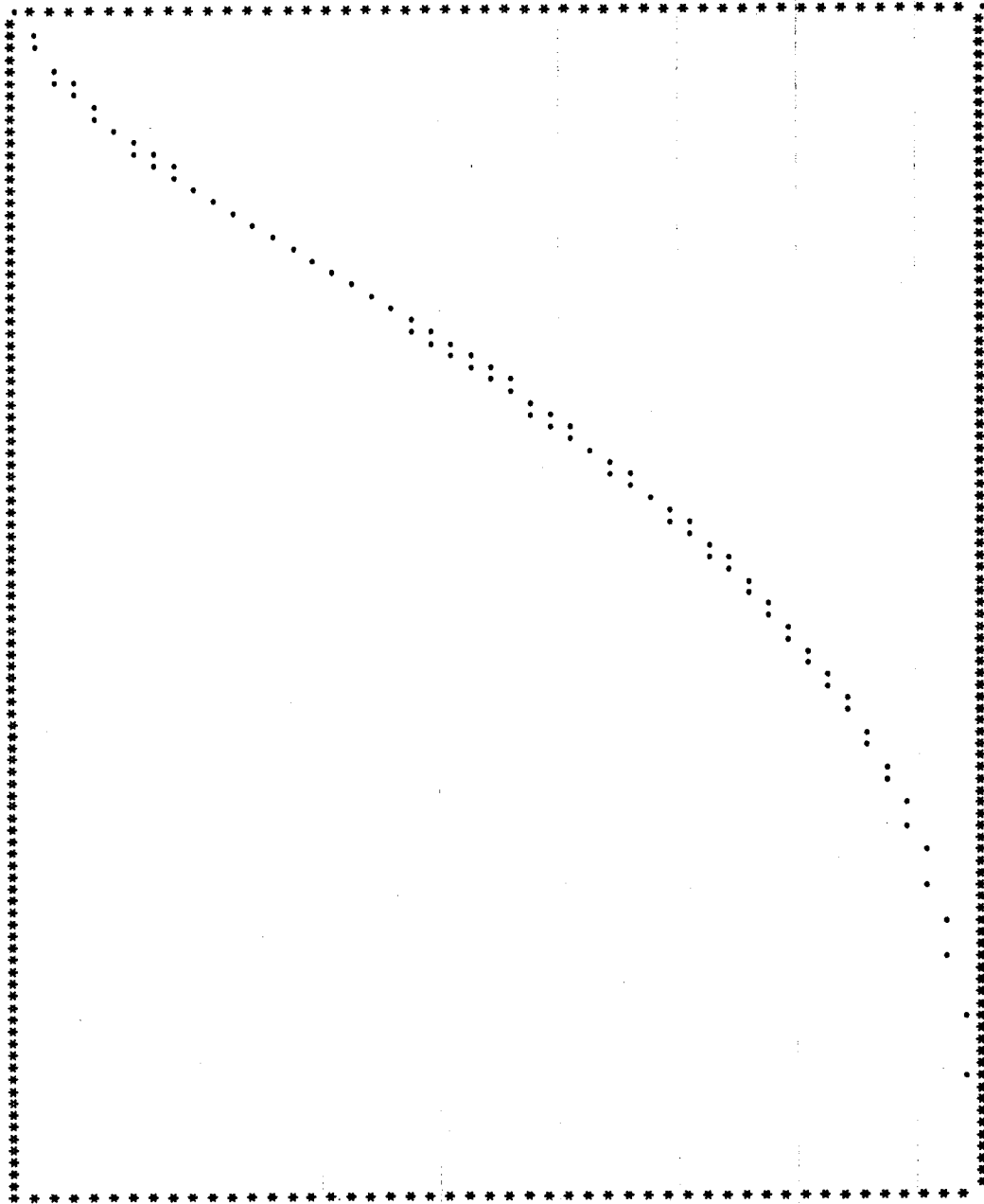
AVERAGE TEMP DERIVATIVE = 0.56306E 01





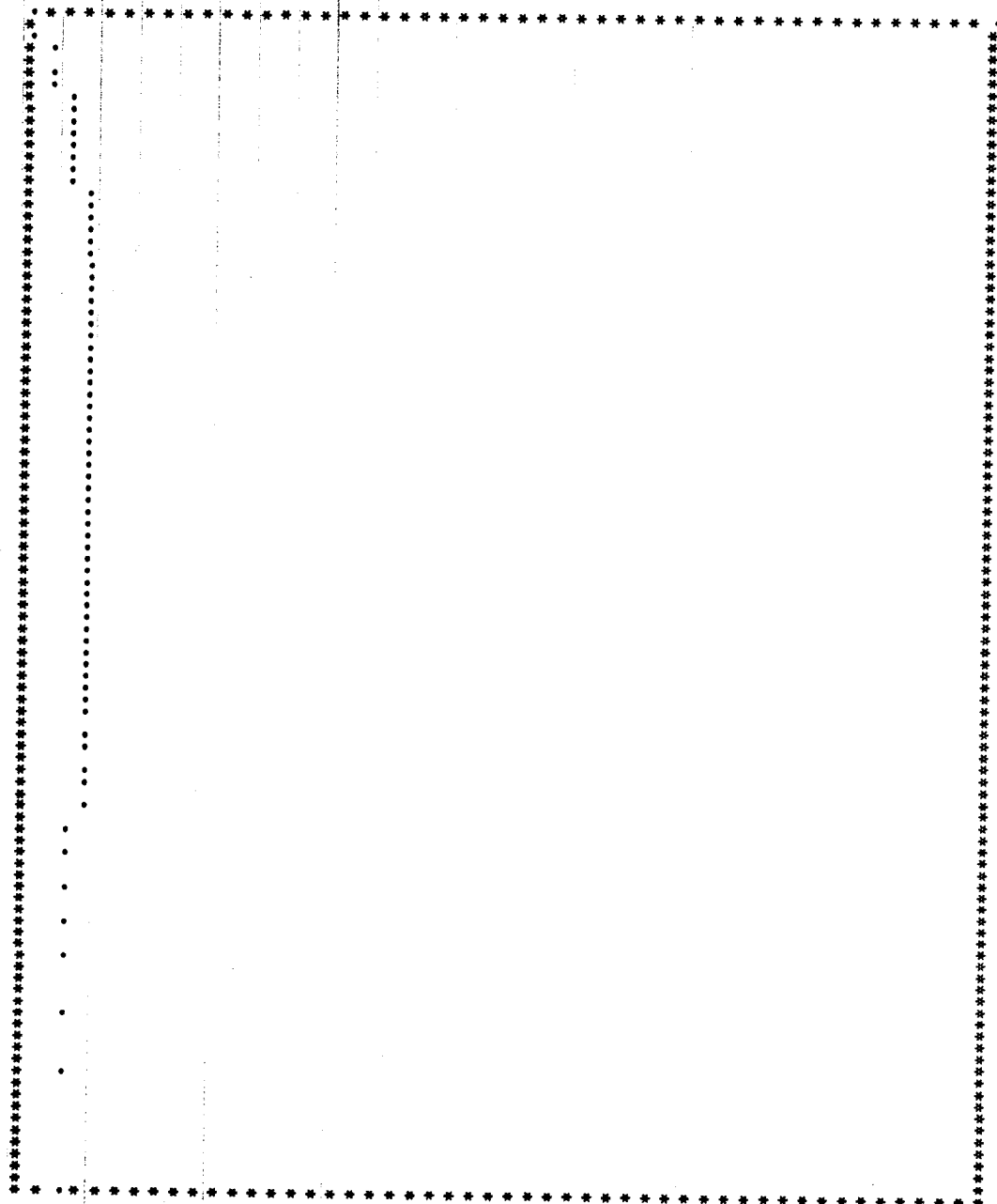
10TF

WEIGHT LOSS VS TIME



XMIN = 0.16009753E 02      XMAX = 0.34826399E 02      YMIN = 0.      YMAX = 0.09999999E 03

TDER VS TIME 10TF



XMIN = 0.16009753E 02 XMAX = 0.34826395E 02 YMIN = 0. YMAX = 0.59709191E 01

APPENDIX VI

RATES OF WEIGHT LOSS OF TEFLON  
UNDER VARIOUS HEATING RATES

TEFLON DEGRADATION

H.R. = HEATING RATE IN DEGREES C PER HOUR  
RATE CF WT. LOSS IN PERCENT PER MINUTE

I.O./H.R.	4TF/ 85		9TF/145		11TF/44		12TF/ 55	
PERCENT	RATE OF	TEMP.	RATE OF	TEMP.	RATE OF	TEMP.	RATE OF	TEMP.
WT.LOSS	WT.LOSS	DEG C	WT.LOSS	DEG C	WT.LOSS	DEG C	WT.LOSS	DEG C
1	0.074	486.5	0.207	494.9	0.069	480.8	0.078	479.9
2	0.210	497.6	0.390	505.3	0.138	489.4	0.154	489.4
3	0.312	503.4	0.553	511.2	0.194	494.5	0.212	494.6
4	0.418	507.6	0.708	515.6	0.243	498.3	0.265	498.5
5	0.526	510.8	0.857	519.0	0.307	501.3	0.323	501.7
6	0.595	513.4	0.998	521.9	0.349	503.6	0.383	504.3
7	0.692	515.8	1.134	524.4	0.403	505.8	0.433	506.6
8	0.776	517.8	1.286	526.6	0.451	507.6	0.504	508.7
9	0.825	519.6	1.412	528.5	0.509	509.2	0.594	510.4
10	0.910	521.3	1.590	530.2	0.563	510.7	0.634	511.9
11	0.987	522.8	1.722	531.8	0.598	512.0	0.637	513.4
12	1.091	524.3	1.811	533.2	0.640	513.3	0.688	514.8
13	1.185	525.5	1.932	534.6	0.688	514.4	0.732	516.1
14	1.239	526.7	2.054	535.8	0.720	515.5	0.789	517.3
15	1.285	527.8	2.193	537.0	0.773	516.5	0.838	518.4
16	1.363	529.0	2.327	538.1	0.805	517.5	0.882	519.5
17	1.451	530.0	2.398	539.2	0.840	518.4	0.921	520.6
18	1.532	530.9	2.513	540.3	0.868	519.3	0.981	521.6
19	1.622	531.9	2.678	541.2	0.948	520.1	1.028	522.5
20	1.704	532.7	2.813	542.1	0.989	520.9	1.066	523.4
21	1.738	533.6	2.873	543.0	1.009	521.6	1.107	524.2
22	1.793	534.4	2.878	543.9	1.023	522.3	1.146	525.1
23	1.887	535.2	2.997	544.7	1.021	523.1	1.207	525.9
24	1.988	535.9	3.119	545.5	1.054	523.8	1.251	526.6
25	2.053	536.6	3.155	546.3	1.086	524.5	1.301	527.4
26	2.122	537.3	3.250	547.0	1.112	525.2	1.311	528.1
27	2.176	538.0	3.359	547.8	1.145	525.8	1.351	528.8
28	2.207	538.6	3.455	548.5	1.159	526.5	1.415	529.5
29	2.236	539.2	3.674	549.2	1.193	527.1	1.443	530.1
30	2.255	539.9	3.812	549.8	1.217	527.7	1.468	530.7
31	2.277	540.5	3.856	550.5	1.246	528.3	1.484	531.4
32	2.327	541.1	3.726	551.1	1.282	528.9	1.526	532.0
33	2.384	541.7	3.888	551.7	1.313	529.4	1.578	532.6
34	2.459	542.3	3.924	552.3	1.334	530.0	1.618	533.2
35	2.537	542.9	4.009	552.9	1.367	530.5	1.670	533.7
36	2.608	543.5	4.060	553.5	1.393	531.1	1.672	534.3
37	2.688	544.0	4.188	554.1	1.413	531.6	1.710	534.9
38	2.754	544.5	4.222	554.7	1.447	532.1	1.749	535.4
39	2.826	545.0	4.286	555.2	1.469	532.6	1.796	535.9
40	2.875	545.5	4.292	555.8	1.489	533.1	1.788	536.4
41	2.912	546.0	4.366	556.4	1.504	533.6	1.792	536.9
42	2.940	546.5	4.400	556.9	1.525	534.0	1.827	537.5
43	2.989	546.9	4.493	557.4	1.538	534.5	1.845	538.0
44	3.014	547.4	4.537	558.0	1.542	535.0	1.846	538.5
45	3.025	547.9	4.603	558.5	1.554	535.4	1.854	539.0
46	3.032	548.3	4.628	559.0	1.564	535.9	1.827	539.5
47	3.035	548.8	4.602	559.5	1.564	536.4	1.861	540.0
48	3.048	549.3	4.706	560.0	1.564	536.8	1.876	540.5
49	3.113	549.7	4.783	560.5	1.564	537.3	1.865	541.0
50	3.114	550.2	4.896	561.0	1.549	537.7	1.856	541.5

## Part II

PERCENT WT.LOSS	RATE OF WT.LOSS	TEMP. DEG C	RATE OF WT.LOSS	TEMP. DEG C	RATE OF WT.LOSS	TEMP. DEG C	RATE OF WT.LOSS	TEMP. DEG C
51	3.128	550.6	4.917	561.5	1.542	538.2	1.869	542.0
52	3.106	551.1	4.903	561.9	1.535	538.7	1.874	542.4
53	3.108	551.5	4.951	562.4	1.521	539.2	1.858	542.9
54	3.106	552.0	4.978	562.9	1.514	539.6	1.838	543.4
55	3.125	552.4	5.055	563.4	1.517	540.1	1.832	543.9
56	3.139	552.9	5.041	563.8	1.513	540.6	1.827	544.4
57	3.146	553.3	5.047	564.3	1.514	541.0	1.898	545.0
58	3.111	553.8	5.120	564.8	1.506	541.5	1.925	545.4
59	3.116	554.2	5.144	565.2	1.504	542.0	1.930	545.9
60	3.100	554.7	5.196	565.7	1.495	542.5	1.890	546.4
61	3.136	555.1	5.185	566.1	1.480	543.0	1.810	546.9
62	3.125	555.6	5.150	566.6	1.463	543.4	1.816	547.4
63	3.113	556.0	5.190	567.0	1.448	543.9	1.776	547.9
64	3.086	556.4	5.179	567.5	1.434	544.4	1.752	548.4
65	3.052	556.9	5.215	567.9	1.425	544.9	1.732	549.0
66	3.014	557.4	5.207	568.4	1.429	545.4	1.763	549.5
67	2.980	557.8	5.138	568.8	1.440	546.0	1.779	550.0
68	2.948	558.3	5.221	569.3	1.437	546.4	1.767	550.5
69	2.935	558.8	5.245	569.7	1.419	546.9	1.714	551.0
70	2.920	559.3	5.270	570.1	1.390	547.4	1.705	551.6
71	2.895	559.8	5.268	570.6	1.379	547.9	1.707	552.1
72	2.862	560.2	5.175	571.0	1.357	548.5	1.716	552.6
73	2.890	560.7	5.108	571.5	1.348	549.0	1.721	553.2
74	2.880	561.2	5.065	571.9	1.361	549.5	1.696	553.7
75	2.861	561.7	4.968	572.4	1.368	550.1	1.686	554.2
76	2.846	562.2	4.933	572.9	1.368	550.6	1.683	554.8
77	2.829	562.7	4.862	573.4	1.368	551.1	1.688	555.3
78	2.779	563.2	4.914	573.8	1.368	551.6	1.743	555.9
79	2.721	563.7	4.949	574.3	1.368	552.1	1.761	556.4
80	2.686	564.2	4.931	574.8	1.368	552.7	1.739	556.9
81	2.631	564.7	4.830	575.2	1.368	553.2	1.730	557.4
82	2.577	565.3	4.666	575.7	1.368	553.7	1.680	557.9
83	2.508	565.8	4.476	576.3	1.368	554.2	1.668	558.5
84	2.514	566.4	4.350	576.8	1.368	554.7	1.637	559.0
85	2.475	567.0	4.204	577.3	1.354	555.2	1.627	559.6
86	2.443	567.5	4.093	577.9	1.354	555.8	1.632	560.1
87	2.411	568.1	3.996	578.5	1.347	556.3	1.614	560.7
88	2.349	568.7	3.851	579.1	1.326	556.8	1.578	561.2
89	2.278	569.3	3.734	579.7	1.303	557.4	1.539	561.8
90	2.218	569.9	3.574	580.4	1.272	557.9	1.489	562.4
91	2.145	570.5	3.442	581.0	1.235	558.5	1.420	563.0
92	2.049	571.3	3.188	581.8	1.196	559.1	1.340	563.7
93	2.009	571.9	3.016	582.5	1.158	559.7	1.255	564.3
94	1.922	572.6	2.845	583.4	1.104	560.3	1.160	565.1
95	1.818	573.4	2.652	584.2	1.028	560.9	1.059	565.9
96	1.664	574.1	2.459	585.2	0.923	561.6	0.946	566.8
97	1.454	575.1	2.180	586.2	0.794	562.5	0.817	567.8
98	1.181	576.1	1.783	587.5	0.608	563.5	0.649	569.0
99	0.827	577.6	1.115	589.2	0.392	564.9	0.429	570.6

APPENDIX VII

COMPUTER PRINTOUT OF ACTIVATION  
ENERGY RESULTS FOR TEFLON DEGRADATION

AFML-TR-68-181  
Part II

XXX FRIEDMANS METHOD FOR EA+A

RUN ID NOS 4TF, 9TF, 11TF, 12TF,

WT LOSS	EA(KCAL)	ST.DEVN.	LOG PREX	ST.DEVN.	AV.LOG AFW	ST.DEVN.	LOG RES.WT.
4	71.285	1.984	19.591	1.192	19.045	0.0188	1.9823
5	69.464	0.758	19.092	0.453	19.058	0.0069	1.9777
6	68.055	1.496	18.697	0.892	19.056	0.0143	1.9731
7	67.468	0.842	18.536	0.501	19.057	0.0096	1.9685
8	66.446	1.263	18.260	0.749	19.063	0.0150	1.9638
9	61.834	2.756	16.991	1.631	19.068	0.0351	1.9590
10	63.575	2.520	17.479	1.488	19.071	0.0302	1.9542
11	66.386	1.741	18.245	1.026	19.060	0.0193	1.9494
12	65.455	1.026	17.989	0.603	19.058	0.0158	1.9445
13	65.037	0.724	17.877	0.426	19.059	0.0156	1.9395
14	64.998	0.898	17.864	0.527	19.055	0.0164	1.9345
15	64.214	1.556	17.650	0.912	19.054	0.0223	1.9294
16	65.039	1.539	17.874	0.900	19.051	0.0204	1.9243
17	64.450	0.962	17.710	0.562	19.046	0.0184	1.9191
18	64.406	0.610	17.698	0.356	19.045	0.0170	1.9133
19	63.620	1.184	17.492	0.690	19.051	0.0219	1.9085
20	64.329	1.210	17.686	0.704	19.050	0.0200	1.9031
21	63.404	1.137	17.427	0.662	19.042	0.0224	1.8976
22	62.178	0.611	17.085	0.355	19.031	0.0243	1.8921
23	63.881	0.488	17.546	0.283	19.028	0.0185	1.8865
24	64.328	0.685	17.669	0.397	19.028	0.0177	1.8808
25	63.056	0.951	17.321	0.551	19.023	0.0226	1.8751
26	64.061	0.951	17.588	0.551	19.017	0.0195	1.8692
27	63.845	0.807	17.527	0.467	19.014	0.0198	1.8633
28	63.977	1.045	17.559	0.604	19.009	0.0204	1.8573
29	65.678	0.670	18.019	0.387	19.008	0.0137	1.8513
30	66.595	0.827	18.261	0.477	19.002	0.0123	1.8451
31	66.057	0.704	18.108	0.406	18.993	0.0127	1.8388
32	62.574	0.384	17.161	0.221	18.984	0.0228	1.8325
33	63.252	0.564	17.345	0.325	18.985	0.0210	1.8261
34	62.930	0.685	17.255	0.394	18.980	0.0222	1.8195
35	62.409	0.806	17.115	0.463	18.979	0.0244	1.8129
36	62.725	0.728	17.194	0.419	18.972	0.0229	1.8062
37	63.605	0.800	17.430	0.459	18.970	0.0207	1.7993
38	62.603	1.059	17.159	0.608	18.966	0.0247	1.7924
39	62.500	1.287	17.130	0.738	18.964	0.0262	1.7853
40	62.142	1.485	17.026	0.851	18.955	0.0231	1.7782
41	62.613	1.515	17.146	0.868	18.947	0.0271	1.7709
42	62.071	1.435	16.996	0.822	18.942	0.0283	1.7634
43	62.932	1.553	17.223	0.888	18.937	0.0265	1.7559
44	63.253	1.555	17.303	0.946	18.927	0.0263	1.7482
45	63.563	1.498	17.376	0.856	18.920	0.0244	1.7404
46	64.112	1.677	17.513	0.958	18.909	0.0242	1.7324
47	63.419	1.507	17.319	0.917	18.899	0.0255	1.7243
48	64.395	1.378	17.573	0.786	18.892	0.0217	1.7160
49	65.801	1.797	17.941	1.024	18.885	0.0217	1.7076
50	67.473	1.644	18.378	0.936	18.875	0.0175	1.6990
51	67.324	1.741	18.488	0.991	18.866	0.0183	1.6902
52	68.027	1.583	18.505	0.901	18.854	0.0164	1.6812
53	69.331	1.665	18.840	0.947	18.843	0.0169	1.6721
54	69.931	1.695	18.988	0.958	18.831	0.0168	1.6628
55	71.029	1.759	19.271	0.999	18.823	0.0186	1.6532
56	71.454	1.906	19.372	1.082	18.812	0.0201	1.6435
57	70.581	1.818	19.134	1.032	18.806	0.0185	1.6335
58	71.095	1.513	19.261	0.858	18.796	0.0159	1.6232
59	71.811	1.533	19.441	0.869	18.787	0.0173	1.6128



AFML-TR-68-181  
Part II

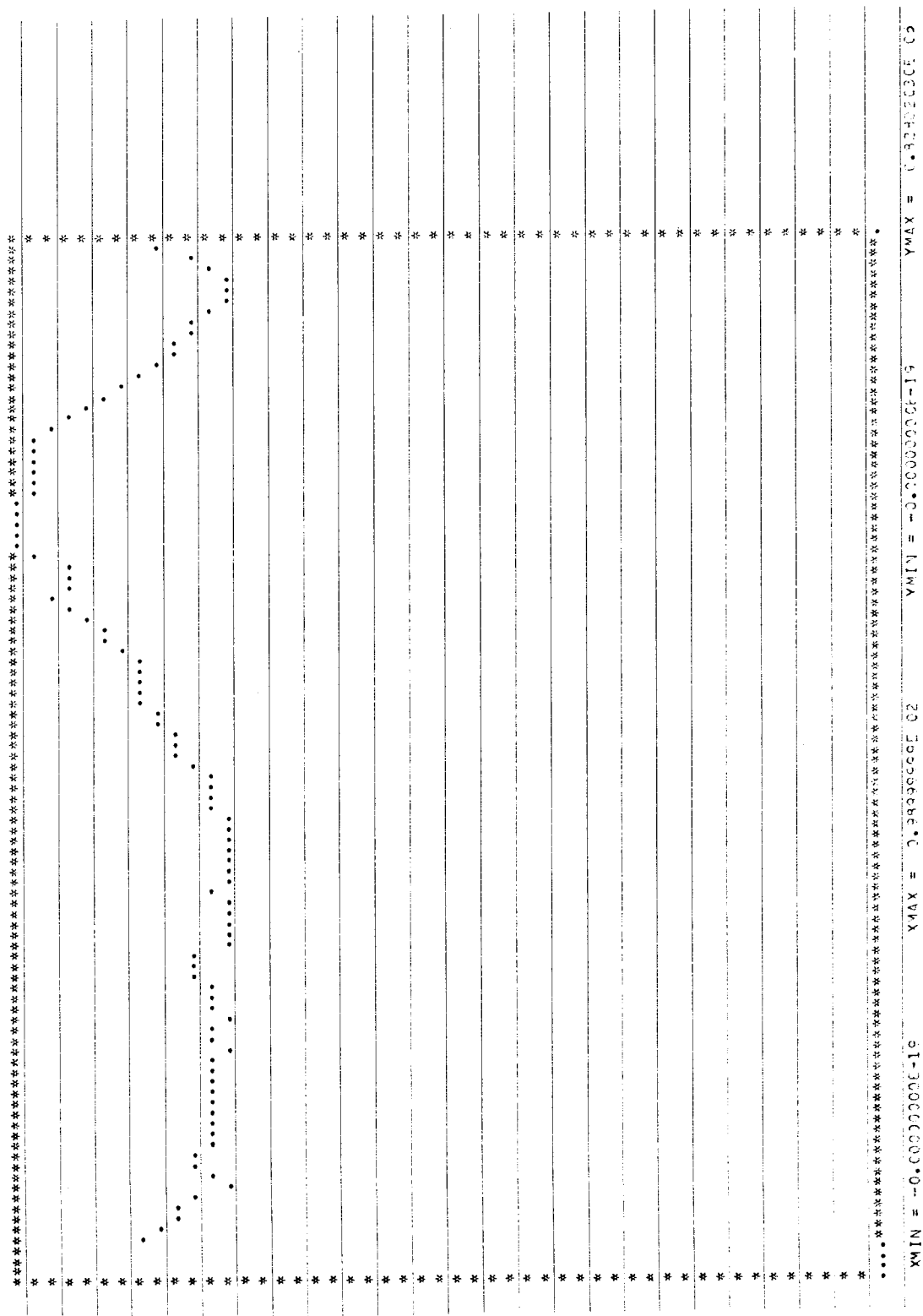
60	73.201	1.384	19.795	0.784	18.774	0.0185	1.6021
61	75.168	1.968	20.301	1.114	18.759	0.0272	1.5911
62	74.993	1.965	20.241	1.112	18.746	0.0267	1.5798
63	76.869	2.105	20.723	1.190	18.733	0.0319	1.5682
64	77.521	2.216	20.880	1.252	18.719	0.0342	1.5563
65	78.950	2.124	21.242	1.200	18.705	0.0371	1.5441
66	78.260	1.632	21.048	0.921	18.695	0.0327	1.5315
67	77.474	1.528	20.828	0.862	18.684	0.0296	1.5185
68	78.446	1.266	21.072	0.714	18.673	0.0313	1.5051
69	80.437	1.562	21.580	0.880	18.658	0.0381	1.4914
70	82.296	1.469	22.054	0.828	18.644	0.0431	1.4771
71	82.603	1.260	22.120	0.709	18.631	0.0433	1.4624
72	82.802	1.074	22.155	0.604	18.616	0.0431	1.4472
73	82.576	1.515	22.081	0.851	18.604	0.0434	1.4314
74	82.425	1.599	22.028	0.898	18.592	0.0430	1.4150
75	81.455	1.733	21.756	0.973	18.577	0.0405	1.3979
76	81.238	1.828	21.685	1.026	18.564	0.0401	1.3802
77	80.322	1.756	21.430	0.984	18.552	0.0373	1.3617
78	80.557	0.855	21.481	0.479	18.543	0.0350	1.3424
79	80.596	0.447	21.478	0.250	18.532	0.0342	1.3222
80	80.958	0.	21.557	0.	18.518	0.0351	1.3010
81	80.003	0.390	21.290	0.218	18.502	0.0322	1.2788
82	78.423	0.804	20.855	0.450	18.482	0.0282	1.2553
83	75.586	0.929	20.092	0.519	18.461	0.0204	1.2304
84	74.344	1.073	19.751	0.599	18.445	0.0179	1.2041
85	72.872	0.996	19.347	0.556	18.426	0.0139	1.1761
86	70.995	0.730	18.841	0.407	18.410	0.0083	1.1451
87	69.734	0.847	18.494	0.472	18.392	0.0079	1.1139
88	68.207	0.881	18.074	0.490	18.369	0.0087	1.0792
89	67.514	1.000	17.869	0.556	18.345	0.0105	1.0414
90	66.070	1.202	17.468	0.669	18.318	0.0147	1.0000
91	66.072	1.541	17.440	0.856	18.289	0.0171	0.9542
92	63.382	2.004	16.704	1.113	18.251	0.0259	0.9031
93	62.757	2.890	16.511	1.603	18.219	0.0334	0.8451
94	62.297	3.752	16.353	2.080	18.178	0.0411	0.7782
95	62.644	4.444	16.397	2.461	18.131	0.0465	0.6990
96	64.330	4.889	16.775	2.705	18.071	0.0487	0.6021
97	65.050	5.001	17.140	2.764	17.991	0.0483	0.4771
98	69.141	5.073	17.817	2.900	17.869	0.0462	0.3010

AVERAGE ACTIVATION ENERGY = 69.343  
AVERAGE LOG PREX = 18.846  
BOTH FOR 10-80 PERCENT WEIGHT LOSS

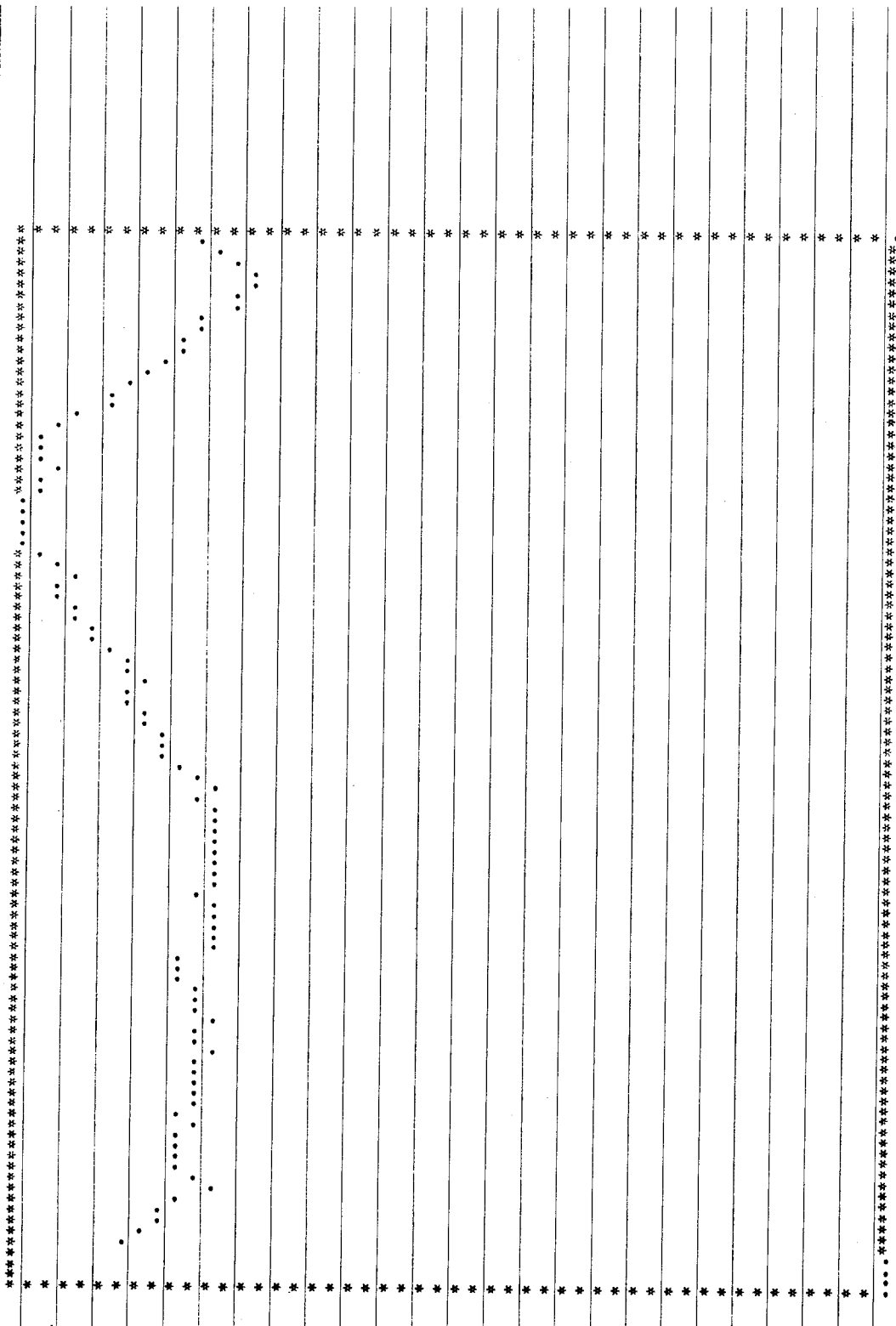
AFML-TR-68-181  
Part II

$XMIN = 0.121512585-02$	$YMAX = 0.124465775-02$	$YMIN = 0.851478075-01$	$YMAX = 0.581107334-03$
-------------------------	-------------------------	-------------------------	-------------------------

ACTIVATION ENERGY VS WEIGHT LOSS



PRE-EXP VS WEIGHT LOSS



AVER LOG AF(W) VS LOG PERCENT WEIGHT REMAINING

[illegible]

```

XMIN = 0.09999999E 01      XMAX = 0.19822712E 01      YMIN = 0.18318354E 02      YMAX = 0.19070782E 02

```

UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>	
		2b. GROUP	
3. REPORT TITLE KINETIC ANALYSIS OF THERMOGRAVIMETRY. PART II. PROGRAMMED TEMPERATURE			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) January 1967 to May 1968			
5. AUTHOR(S) (First name, middle initial, last name) Goldfarb, Ivan J., McGuchan, Robert, and Meeks, Alan C.			
6. REPORT DATE November 1968		7a. TOTAL NO. OF PAGES 86 77	7b. NO. OF REFS 40
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-68-181, Pt II	
b. PROJECT NO. 7342			
c. Task No. 734203		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson AFB, Ohio	

## 13. ABSTRACT

< A generally applicable method of obtaining kinetic parameters from temperature-programmed thermogravimetry is presented. Factors influencing the selection of a particular method for the numerous treatments reported in the literature are discussed in detail. The method of Friedman involving the use of several thermograms at different heating rates and determining Arrhenius parameters at each percent conversion was chosen. The experimental procedure and a method of handling thermogravimetric analysis (TGA) data and calculations by computer are fully described. The application of the treatment to some specific polymer degradation systems is reported in order to illustrate the scope of the method and its potential usefulness in obtaining information concerning complex degradation mechanisms. Poly(tetrafluoroethylene), an aliphatic, and an aromatic polyamide were the polymers selected for this study. >

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermogravimetry TGA Kinetics Degradation Polymer						

UNCLASSIFIED

Security Classification